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Ambient Monitoring Aloft of Ozone and Precursors Near and Downwind of St. Louis

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AMBIENT MONITORING ALOFT OF OZONE AND PRECURSORS NEAR AND DOWNWIND OF ST. LOUIS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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Experimental protocol accompanying the launching and flight of a manned balloon (Project DaVinci II) to measure primary and secondary pollutants is described. Measurements obtained concurrently beneath the balloon at the earth's surface are also described. The flight occurred on June 8-9, 1976, days characterized by atmospheric stagnation. The data indicate that ozone trapped aloft by a nocturnal inversion decays slowly. Transport of ambient ozone at levels exceeding the Federal Air Quality standard is documented for over 150 mil downwind of St. Louis. These observations strongly support the contention that, in at least some instances, high levels of rural ozone are importantly influence by long range transport from urban areas.

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by

C.E. Decker, J.J.B. Worth, L.A. Ripperton, and W.D. Bach

Research Triangle Institute
Research Triangle Park, North Carolina 27709

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EPA Project Officer: Edwin L. Meyer, Jr.

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Office of Air and Waste Management
Office of Air Quality Planning and Standards
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January 1977

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ABSTRACT

The objectives of this project were to collect air chemistry data in a Lagrangian frame of reference and to provide quality control for measurements during the Project DaVinci II flight. Project DaVinci II was a balloon-borne air chemistry experiment sponsored by ERDA and conducted in the vicinity of St. Louis during the period June 8 to June 9, 1976. Measurements of constituents (e.g., O_3, NO_x, SO_2, $SO_4^=$, and hydrocarbon compounds) and meteorological variables were conducted onboard the DaVinci II system and at ground level utilizing several chase vehicles, including the RTI Environmental Monitoring Laboratory. The DaVinci II balloon was launched from Arrowhead Airport, at 0857 on June 8, 24 kilometers west of St. Louis. For the next 24 hours the balloon drifted south, then turned north, and finally eastward across the southern Illinois plains before landing at 0905 on June 9 in a wheatfield in southwestern Indiana.

Ozone concentrations measured at flight altitude ($\approx$ 800 m) during the nocturnal portion of the flight ranged from 230 to 290 $\mu g/m^3$ until the monitor was turned off at 0700 the next morning. Ozone concentrations at the ground showed a rapid decrease with nightfall to a minimum of approximately 60 $\mu g/m^3$. General meteorological conditions--a subsidence inversion aloft and a strong radiative inversion based at the ground--were nearly ideal for long distance transport aloft of ozone and precursors at night. The occurrence of high ozone concentrations (> 250 $\mu g/m^3$) on the morning of June 9 in a rural area in southwestern Indiana was attributed to long-distance transport of ozone in an urban plume from St. Louis, Missouri. This report is based on a preliminary examination of ozone data collected during the DaVinci II flight. A more detailed analysis and evaluation of all data collected during the flight will be conducted in the near future under a separate contract.

ACKNOWLEDGMENTS

This project was conducted by Research Triangle Institute (RTI), Research Triangle Park, North Carolina, under Contract No. 68-02-2391 for the United States Environmental Protection Agency. The support of this agency is gratefully acknowledged as is the advice and guidance of the Project Officer, E. L. Meyer, Jr., and other staff members of the Office of Air Quality Planning and Standards.

Work on this project was performed by staff members of the Systems and Measurements Division of RTI under the general direction of Mr. J. J. B. Worth, Group III Vice President. Mr. Worth was Laboratory Supervisor for this program. Mr. C. E. Decker served as Project Leader and was responsible for the coordination and conduct of the program. Staff members of RTI who contributed to the field measurement program and to the preparation of this report are listed in alphabetical order: Dr. W. D. Bach, Mr. C. E. Decker, Mr. R. B. Denyszyn, Mr. R. W. Murdoch, D. L. A. Ripperton, Mr. J. A. Scheibe, and Mr. J. J. B. Worth.

1.0 INTRODUCTION

1.1 Background

Previous studies of nonurban ozone concentrations have led to the conclusion that nonurban ozone is significantly affected by long-range transport of ozone (refs. 1,2). These studies have suggested that the unique precursor, synthesis, destruction, and transport conditions within a high-pressure system are conducive to the transport of ozone in large concentrations for long distances. At night the radiative temperature inversion develops, stabilizes the air, and inhibits vertical transfer processes. The inversion effectively insulates the ozone aloft from destruction by contact with the surface or by reaction with ozone-destructive agents (NO, NO_2) that may be emitted near the ground. Overnight, the air is transported further downwind and diffused horizontally. With the advent of solar heating, the radiative inversion is destabilized from the ground up while ozone is being synthesized, until the inversion is broken. Vertical mixing is no longer inhibited and ozone-rich air from aloft may be brought to the ground.

The role of urban ozone and its interactions with rural air quality background levels through transport and diffusion is important for strategy decisions relating to regional air quality control. One of the specific questions yet to be answered is, "How do urban ozone and associated precursors affect the observed high levels of rural oxidant?" The basic strategy question is whether urban hydrocarbon control will affect oxidant concentrations equally in the city and in the downwind rural areas.

To examine the question of urban transport, it is necessary to trace or move with an air parcel from a highly urban background into a "relatively clean" rural location. An opportunity for such a definitive field experiment existed this summer in association with a scheduled ERDA (Energy Research and Development Administration) experiment, Project DaVinci II.

Project DaVinci II was a manned, balloon-borne scientific experiment conducted in St. Louis, Missouri, in early June to study the behavior of air pollutants in the lower atmosphere. The primary emphasis of the experiment was focused upon the chemical processes by which gaseous effluents from urban areas are transformed into more hazardous pollutants in the atmosphere

while being transported away from an urban area. Studies of the transformation of gaseous SO_2 into sulfate (SO_4) aerosols in the presence of other gases were the principal justification for the flight. Measurements of ozone and ozone precursors in the urban plume were also made to determine changes in their relative proportions in space and time as the balloon drifted nearly with the wind.

The balloon-borne measurement program provided an excellent opportunity to investigate the atmospheric chemistry associated with the long-distance transport of ozone. It offered these distinct advantages:

(1) Air quality measurements could be made in a Lagrangian frame of reference (i.e., within a moving air parcel).

(2) The results of chemical processes occurring in an urban air parcel could be continuously monitored over the time interval of transport.

(3) Continuous airborne sampling could be conducted within a layer of air bounded aloft by the subsidence inversion and below by the ground-based radiation inversion.

(4) This experiment provides the needed data to uniquely document the contribution of a single city's effluvia to the background pollution levels within a given air parcel.

1.2 Objectives

The primary objective of the EPA-RTI participation in Project DaVinci II was to document the role of urban ozone transport and its interactions with rural air quality background levels by the collection of air chemistry data in a Lagrangian frame of reference. The secondary objective was to provide quality control for air quality measurements during the experiment.

2.0 PROJECT DaVINCI II

The DaVinci II system consists of a double-decked gondola approximately 3 meters square; a 22-m suspension harness that connects the gondola with the 22-m-diameter balloon; power bay, instrumentation, and telemetry systems; data receiving systems for the chase vehicles; and navigational and life support equipment for a crew of four. The payload can be as much as 2955 kg using the gondola and balloon described. The system was designed to permit several days of flight for a crew of four with approximately 909 kg of scientific equipment and power supply onboard.

The flight used an especially worthy and proven balloon (figure 1) that is constructed of a double layer of clean, 2-mil polyethylene and that has a nominal volume of about 186,000 ft^3. It has a diameter of about 22 m, a gore length of 36 m, and 49 load-bearing tapes of 450 kg test. Helium was used as the lifting gas. Two valves at the balloon apex were operated on separate electrical systems to vent helium as needed to assist in controlling the altitude of the balloon. Figure 1 is a picture of the inflated balloon and gondola just prior to launch.

The gondola was constructed by the Grumman Aircraft Corporation and certified as airworthy by FAA. It is 3 m square and double tiered. It was especially designed to protect crew and equipment in event of rough landing and yet be used again. The lower deck has about 1 m of head room and is used for batteries, supplies, ballast, life support equipment, and crew sleeping quarters. The upper deck is fiberglass and is used for flight operations and for conducting the scientific experiments. The bottom of the gondola is equipped with a layer of about 0.5-m thickness of impact material or "crush pads" to provide shock absorption in landings. Scientific equipment is located throughout the flight train. A closeup photograph of the gondola and supporting scientific instrumentation is shown in figure 2.

2.1 Air Quality Measurements

2.1.1 DaVinci II Measurements

The following measurements applicable to the study of atmospheric ozone or ozone precursors were made aboard the gondola of the balloon system by

Figure 1. DaVinci II balloon and gondola.

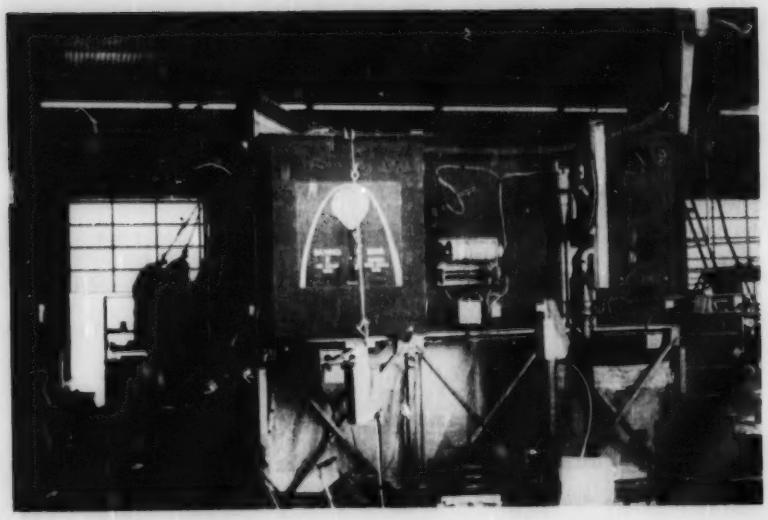

Figure 2. Photograph of gondola and scientific equipment.

the indicated participating organization*:

Spectrometer measurements of ultraviolet and visible solar flux (SL), ozone (SL, ASL); grab samples for post-flight analyses of CO, N_2O (SL), light hydrocarbons, C_2 to C_6, and halocarbons (SL, RTI, WSU); temperature, pressure, water vapor (ASL); relative air velocity (AVC).

Ozone concentration measurements (ASL) and eddy diffusivity measurements (AVC) were made on an unmanned "down package" suspended below the gondola.

The project protocols called for aircraft measurements of SO_2, O_3, NO, NO_2, SO_4, temperature, dew point temperature, eddy diffusivity and condensation nuclei by Washington University (St. Louis). These measurements were intended to describe the areal variability of the environment about the moving gondola.

At the ground level, a pair of acoustic sounders (Argonne National Laboratory) followed and anticipated the track of the balloon in a leap-frog fashion to measure the thermal structure of the planetary boundary layer. The RTI mobile van, instrumented to measure O_3, NO, NO_2, SO_2, THC, CH_4, and CO and temperature, followed the balloon track from launch to landing, and provided calibration of the balloon instrumentation before and after the flight.

2.1.2 RTI Measurements

2.1.2.1 Ground Level Measurements

Continuous ozone, nitrogen oxide (NO, NO_x), and sulfur dioxide measurements and continual (i.e., once every 5 minutes) measurements for THC, CH_4, and CO were made aboard the RTI Environmental Monitoring Laboratory (RTI-EML) for an approximately 16-day period prior to the launch of the DaVinci II balloon and during the actual flight. For that period, the RTI-EML was parked at Arrowhead Airport, located approximately 24 kilometers west of St. Louis. Sample air was aspirated through a Teflon tube-glass manifold system from a height of 10 m. Figure 3 shows the RTI-EML onsite at Arrowhead Airport prior to the launch of DaVinci II. During the in-transit measurement

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*SL - Sandia Laboratories; ASL - U.S. Army Atmospheric Sciences Laboratory; WSU - Washington State University; AVC - AeroVironment Corporation.

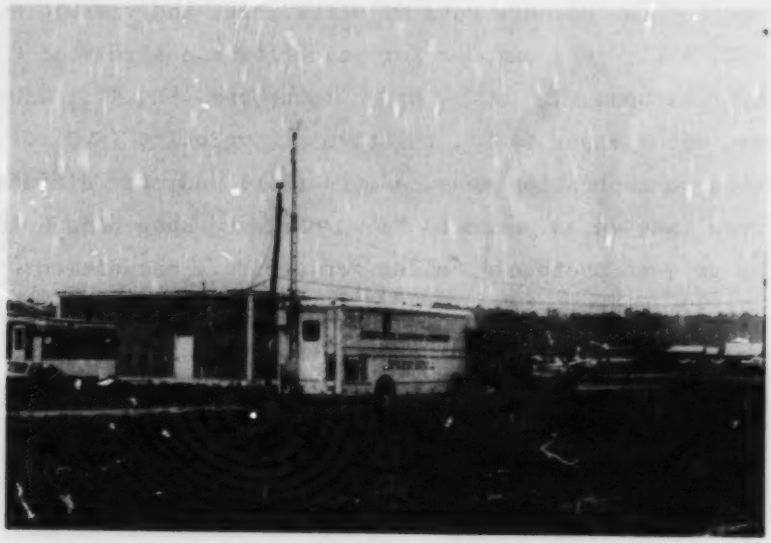

Figure 3. RTI Environmental Monitoring Laboratory onsite at Arrowhead Airport.

period, sample air was provided to the instruments through a Teflon-glass manifold. Its inlet was located approximately 3.5 m from the ground and extended 1 m in front of the RTI-EML. Theoretical calculations and extensiv road tests were conducted to insure that effects due to aerodynamic characteristics of the RTI-EML and vehicular exhausts on the ambient air sample were minimized. A minimum flow of 0.1 m^3/min was maintained through the manifold at all times.

Instrumentation and calibration procedures used to obtain ambient air measurements prior to the flight and in transit during the flight for the above mentioned pollutants are summarized in table 1. Appropriate quality control procedures and sufficient instrument calibrations were performed to obtain high quality data. Quality control procedures included verification of calibration procedures, standards, and operating procedures; performing dynamic calibrations and checks; maintaining adequate records to describe instrument performance; and thorough training of the instrument technicians.

Table 1. Instrumentation and calibration procedures

Parameter	Instrument	Calibration procedure
O_3	Bendix Chemiluminescent	NBKI Method; Gas Phase Titration
SO_2	Thermo-Electron Pulsed-Fluorescent	NBS Permeation Tube
NO, NO_x	Bendix Chemiluminescent	NBS SRM (NO in N_2) Gas Phase Titration for NO_x
THC, CH_4, CO	Beckman 6800 Air Quality Chromatograph	CH_4 and CO in certified cylinders (aluminum construction)

2.1.2.2 Balloon-Borne Measurements

Instrumentation and equipment were installed on board the DaVinci gondola by RTI for the collection of integrated samples in Tedlar bags at hourly intervals for subsequent selected hydrocarbon and halocarbon analyses at RTI.

Detailed hydrocarbon analyses were performed on grab samples collected during the flight of DaVinci using a modified Perkin-Elmer Model 900 gas chromatograph coupled to a Hewlett-Packard Model 2100A computer. Ten hydrocarbons were analyzed:

ethylene/ethane	n-butene
acetylene	1-butene
propane	trans-2-butene
propylene	isopentane
isobutane	cyclopentane

Separation of the C_2-C_5 hydrocarbons were made on a 1.8-m x 0.15-cm i.d. Durapak n-octane (100-120 mesh) column that was operated at 23° C. The sum of the 10 nonmethane hydrocarbons analyzed above was computed for each

grab sample collected on board the DaVinci II system and is hereafter referred to as Σ NMHC. Methane and carbon monoxide concentrations were measured on each grab sample using a Beckman 6800 Air Quality Chromatograph.

Freon 11 and Freon 12 analyses were performed on grab samples collected during the DaVinci flight using a Perkin-Elmer Model 900 gas chromatograph with electron-capture detector. These compounds were separated on a 2-m glass column packed with Chromosorb W-H.P. and coated with 10 percent DC-200.

2.2 Flight Description

On June 8, 1976, at 0857 CDT, the DaVinci II balloon was launched from Arrowhead Airport, 15 miles west of St. Louis, Missouri. For the next 24 hours the balloon drifted south, then turned north, and finally eastward across the southern Illinois plains before landing in a wheatfield in southwestern Indiana (see figures 4 and 5). Figure 4 shows the flight track of the DaVinci II balloon for the first 12 hours in and about the St. Louis area. Figure 5 shows the entire flight track of the balloon from launch at Arrowhead Airport to touchdown in Indiana. The flight ended at 0905 CDT on June 9, 1976. During the flight, airborne air chemistry and meteorological measurements were made aboard the main manned gondola and an unmanned "down package" suspended 61.5 m below the gondola. Several supporting aircraft, acoustic sounders, and a mobile van followed the balloon, gathering air quality and meteorological data at flight level and at ground level beneath the gondola.

During the 24-hour flight, the RTI-EML was used to obtain measurements of ozone, nitrogen oxides, sulfur dioxide, total hydrocarbons, methane, and carbon monoxide at ground level approximately along and underneath the balloon track. Figures 6 and 7 show ground tracks for the RTI-EML plotted on the same scale as those for the balloon track shown in figures 4 and 5. With the exception of a 2-1/2 hour period of time early in the morning (≈ 0300 to 0600) on June 9, 1976, the RTI-EML was in visual and radio contact with the DaVinci II balloon. At the conclusion of the flight (0905 CDT, June 9, 1976), the RTI-EML was within 0.8 km of the landing site. The RTI-EML was then brought adjacent to the DaVinci balloon for postcalibration of the Dasibi ozone monitor that was flown aboard the balloon (figure 8).

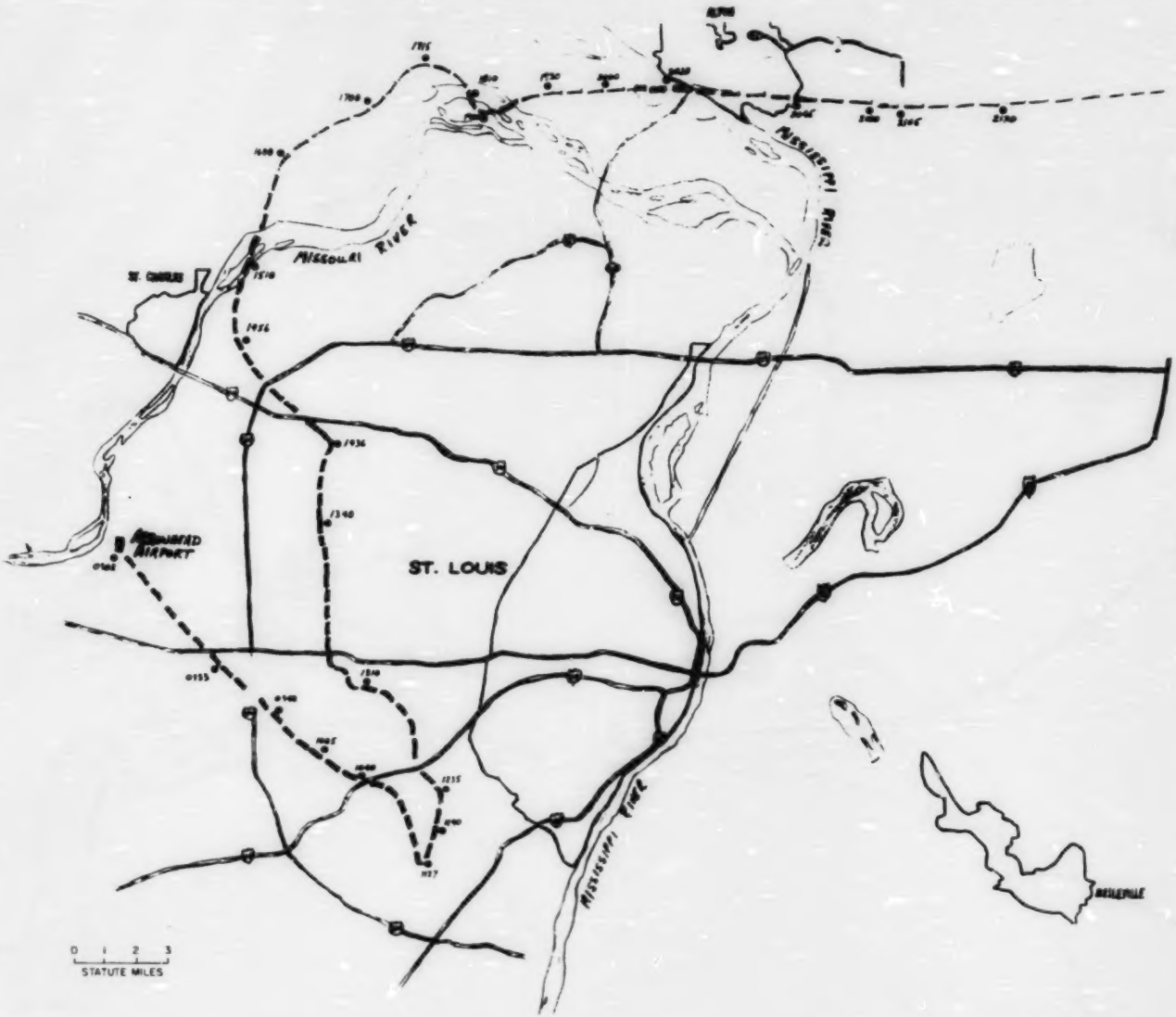

Figure 4. DaVinci II flight track - June 8 (0857) to June 8 (2120), 1976.

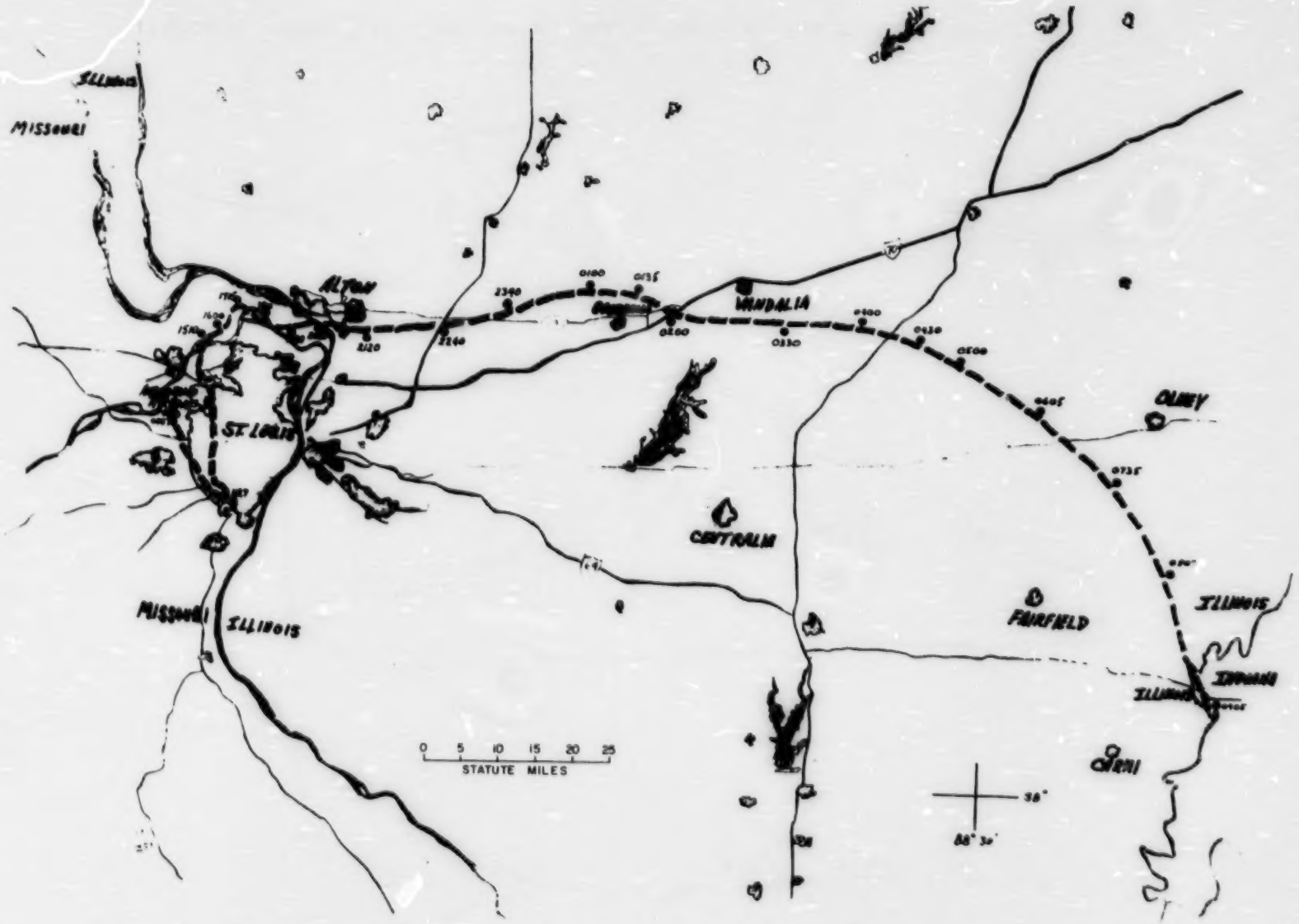

Figure 5. DaVinci II flight track - June 8 (0857) to June 9 (0905), 1976.

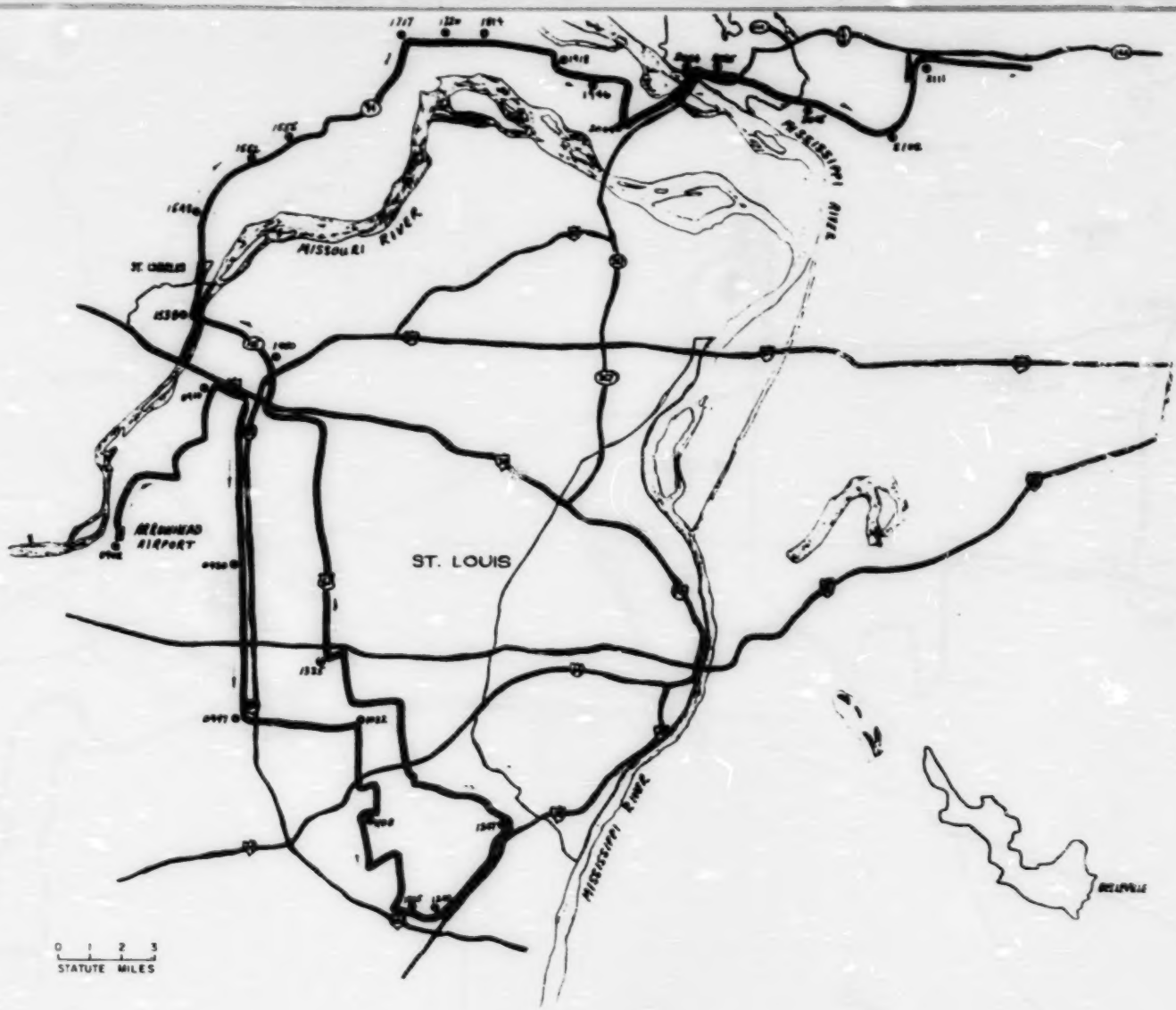

Figure 6. RTI mobile van track - June 8 (0902) to June 9 (2111), 1976.

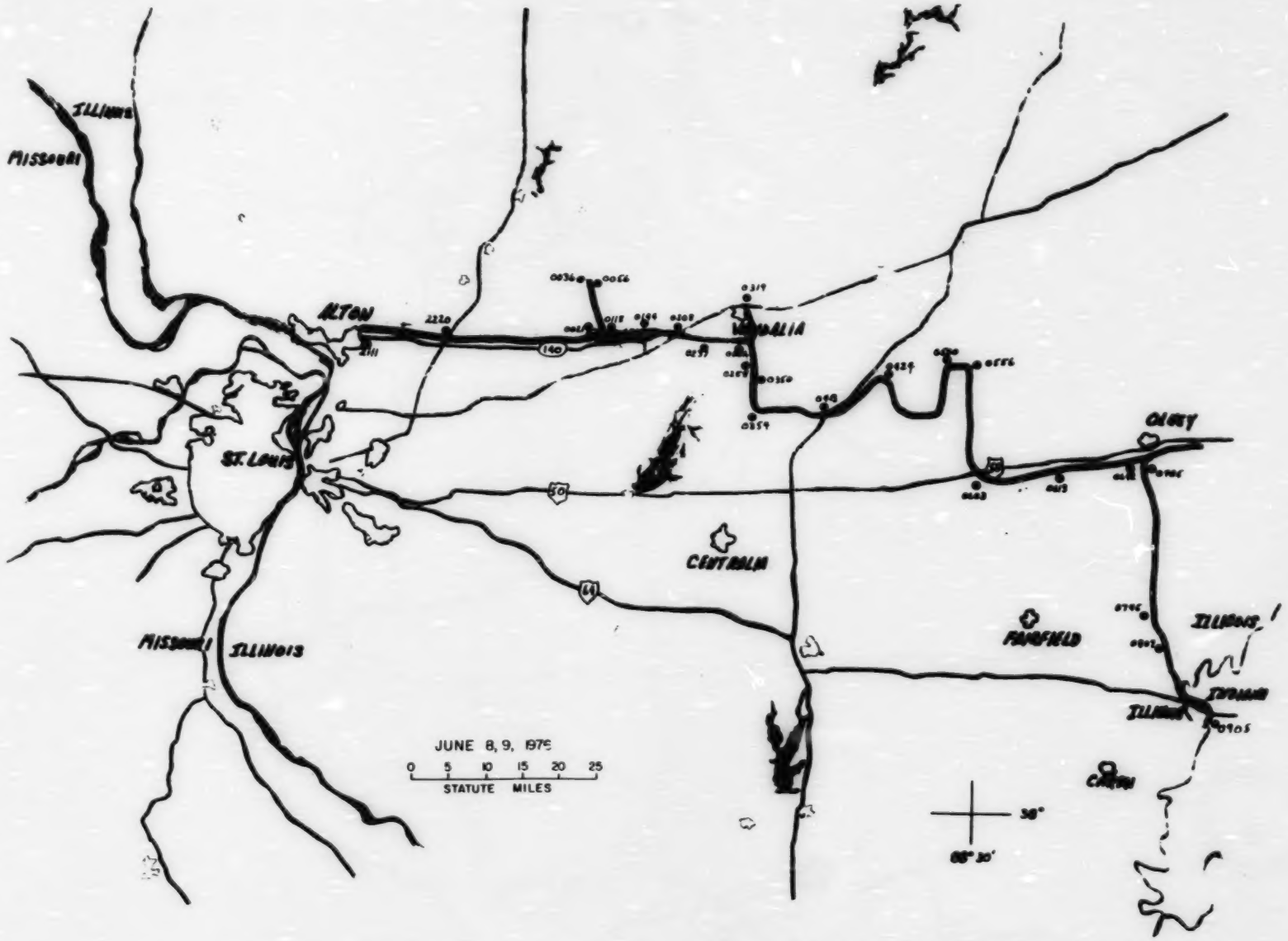

Figure 7. RTI mobile van track - June 8 (2111) to June 9 (0905), 1976.

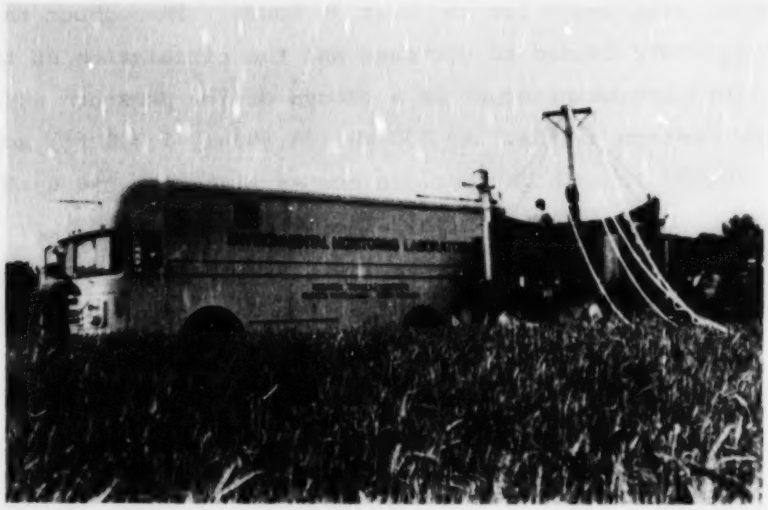

Figure 8. RTI mobile van located adjacent to gondola for post-flight calibration of DaVinci II analyzers.

Postcalibration of the analyzer indicated that the analyzer response was within 3 percent of the preflight calibration.

Each participating organization in Project DaVinci II is responsible for prompt analysis and interpretation of its own experimental data. A central clearing point for transfer of data among participants has been established to facilitate the data exchanges. Since data availability is beyond the control of RTI, the only data included in this report are the air quality data obtained aboard the RTI-EML and the results of hydrocarbon and halocarbon analyses on grab samples collected aboard the balloon.

2.3 Meteorological Considerations

For several days prior to the DaVinci II flight, a high pressure system dominated the circulation of the midwestern United States. From a position near Vandalia, Illinois, at 0300 on June 7, the high center drifted west southwestward over St. Louis at 0900 on June 7 enroute to the Springfield, Missouri, area, arriving there at 0300 on the morning of June 8. The system

remained nearly stationary for the next 36 hours. Throughout this period the central pressure tended to decrease and the circulation on the north and western portions became stronger as a trough of low pressure advanced eastward from the western plains. At 850 mb, (1,500 m, 5,000 ft) and at 700 mb (~ 3,000 m, 10,000 ft) a high pressure center also migrated to the south southwestward with the surface high. The persistence of a high pressure system aloft helped keep skies of the lower atmosphere clear, enhancing radiational cooling at the ground. Nighttime temperatures at weather stations in southern Illinois fell to the 13-16° C range on the night preceding the flight and the night of the flight. Those temperatures, coupled with afternoon temperatures 11° C higher, indicate strong radiational cooling at night and an active, unstable boundary layer during the day.

The surface winds at Lambert Field (St. Louis) shifted from an easterly component through calm and into a westerly and southwesterly direction as the high pressure center moved across the area. After 0900 June 8, surface winds at Lambert Field remained out of the southwest at 5 knots. At launch time, winds at the ground over southern Illinois were northwesterly to northerly, with the high center near Springfield, Missouri. Six hours later, wind flow was poorly defined as the area lay in a ridge of high pressure. Nighttime circulation patterns at the ground suggest a weak (< 5 knots), anticyclonic flow from the north through northwest.

The Salem, Illinois, rawinsonde station, 80 km east of St. Louis, showed a northeasterly wind at 5 knots at 850 mb (1,558 m) 2 hours before launch time. At 1900 CDT, on June 8, the wind turned to the north and increased in speed to 10 knots. By the morning of June 9, the wind direction at Salem had reversed, becoming south southwest at 10 knots at 850 mb. Special rawinsonde releases were made at hourly intervals at the Peoria and Salem, Illinois locations. Those data have not been obtained yet, but should contain greater detail on the structure of the planetary boundary layer.

3.0 PRELIMINARY RESULTS

Prior to the launch of the DaVinci II balloon, approximately 16 days of background data were obtained at the Arrowhead Airport. The data show that the NAAQS for photochemical oxidants was exceeded on numerous occasions. A synopsis of these data is as follows:

(1) Fifty-nine hours of the 384 hours of data (i.e., 15.5 percent) exceeded the NAAQS for photochemical oxidants, (i.e., $\geq$ 160 $\mu g/m^3$).

(2) Ozone concentrations ranged from a measured zero to a maximum hourly average of 293 $\mu g/m^3$. The mean hourly ozone concentration was 98 $\mu g/m^3$.

(3) Ozone exceeded the NAAQS every day from June 1 to launch with 8, 3, 5, 1, 3, 10, and 11 hours exceeding the NAAQS for the days June 1 to 7, respectively.

Oxides of nitrogen (NO and NO_x) concentrations were generally low during this period of time. Nitric oxide concentrations ranged from a measured zero to a maximum hourly average concentration of 70 $\mu g/m^3$. The mean hourly NO concentration for the 16-day period was 5 $\mu g/m^3$. The NO_x concentration ranged from a measured zero to 130 $\mu g/m^3$, with a mean hourly concentration of 19 $\mu g/m^3$. Sulfur dioxide concentrations ranged from a measured zero to 220 $\mu g/m^3$, with a mean SO_2 concentration of 52 $\mu g/m^3$. Hourly average total hydrocarbon, methane, and carbon monoxide concentrations were 1193, 1107, and 611 $\mu g/m^3$, respectively, for the period. The hourly average nonmethane hydrocarbon concentration for the period was 86 $\mu g/m^3$. Air quality data for this period of time are presented in tabular form in appendix A.

Hourly average ozone concentrations obtained at Arrowhead Airport are plotted in figure 9 for the first 8 days of June. Data presented show several days (i.e., June 2 to June 4) where maximum hourly average ozone exceeded the NAAQS and a relatively high minimum ozone concentration remained overnight. Wind direction measurements indicated flow from the west and north (i.e., general flow over rural and suburban areas). Precursor concentrations, i.e., NO_x and hydrocarbons, generally peaked around 10 o'clock in the morning, decreased during the afternoon hours, and increased again, reaching a maximum about midnight. On June 6 and 7, the wind shifted to the southeast with flow

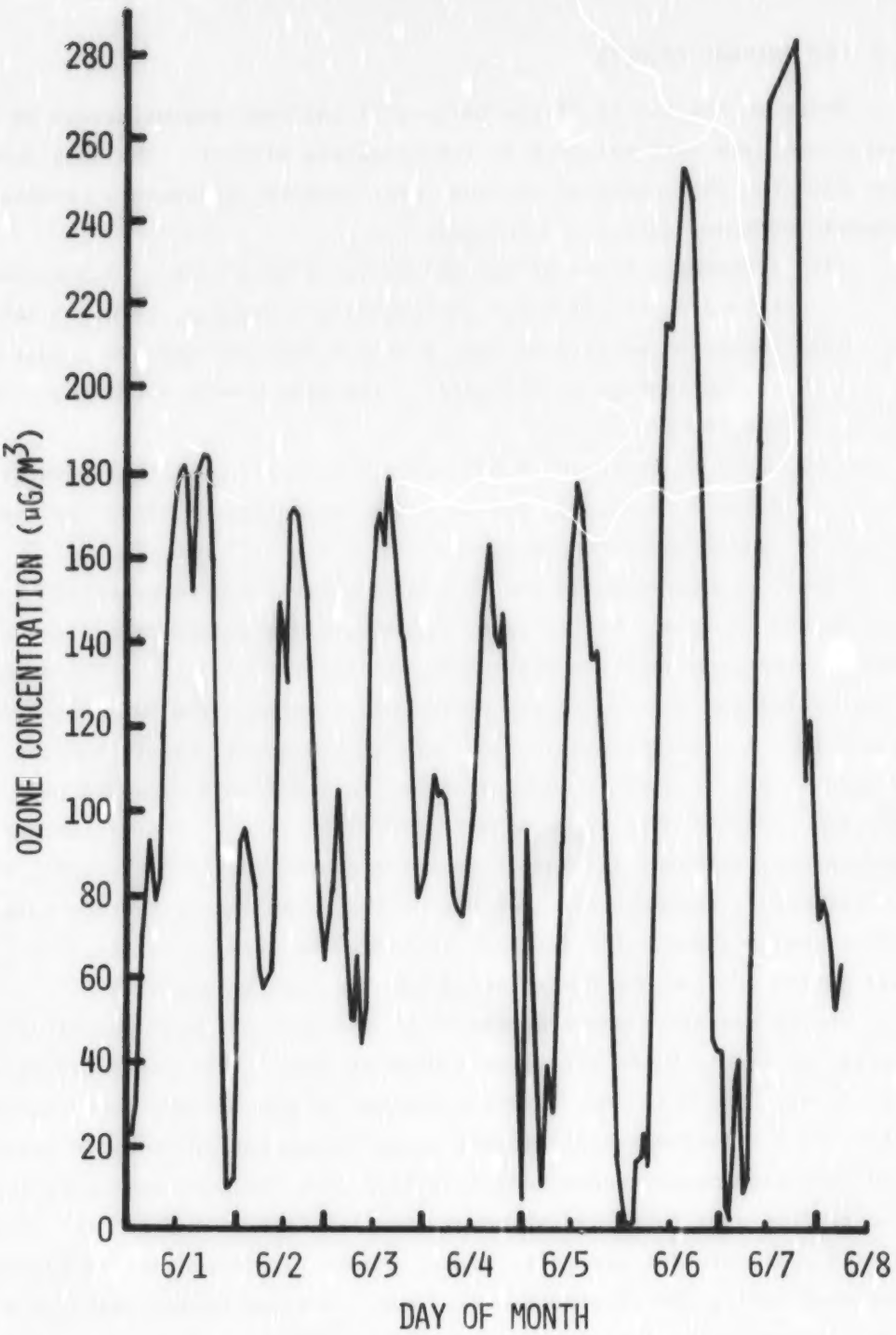

Figure 9. Hourly average ozone concentration at Arrowhead Airport (June 1 to June 8, 1976).

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(2) Ozone concentrations ranged from a measured zero to a maximum hourly average of 293 $\mu g/m^3$. The mean hourly ozone concentration was 98 $\mu g/m^3$.

(3) Ozone exceeded the NAAQS every day from June 1 to launch with 8, 3, 5, 1, 3, 10, and 11 hours exceeding the NAAQS for the days June 1 to 7, respectively.

Oxides of nitrogen (NO and NO_x) concentrations were generally low during this period of time. Nitric oxide concentrations ranged from a measured zero to a maximum hourly average concentration of 70 $\mu g/m^3$. The mean hourly NO concentration for the 16-day period was 5 $\mu g/m^3$. The NO_x concentration ranged from a measured zero to 130 $\mu g/m^3$, with a mean hourly concentration of 19 $\mu g/m^3$. Sulfur dioxide concentrations ranged from a measured zero to 220 $\mu g/m^3$, with a mean SO_2 concentration of 52 $\mu g/m^3$. Hourly average total hydrocarbon, methane, and carbon monoxide concentrations were 1193, 1107, and 611 $\mu g/m^3$, respectively, for the period. The hourly average nonmethane hydrocarbon concentration for the period was 86 $\mu g/m^3$. Air quality data for this period of time are presented in tabular form in appendix A.

Hourly average ozone concentrations obtained at Arrowhead Airport are plotted in figure 9 for the first 8 days of June. Data presented show several days (i.e., June 2 to June 4) where maximum hourly average ozone exceeded the NAAQS and a relatively high minimum ozone concentration remained overnight. Wind direction measurements indicated flow from the west and north (i.e., general flow over rural and suburban areas). Precursor concentrations, i.e., NO_x and hydrocarbons, generally peaked around 10 o'clock in the morning, decreased during the afternoon hours, and increased again, reaching a maximum about midnight. On June 6 and 7, the wind shifted to the southeast with flow

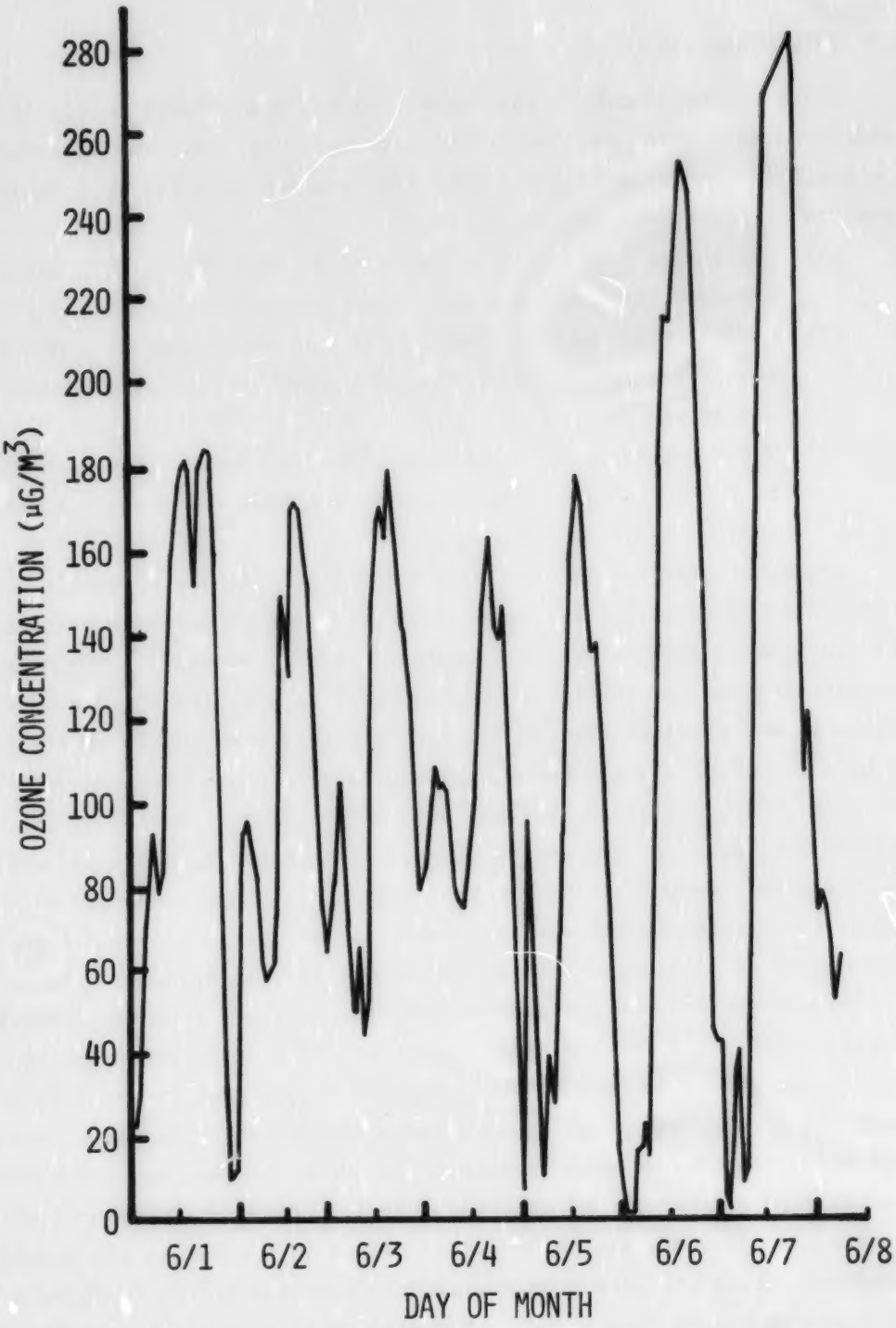

Figure 9. Hourly average ozone concentration at Arrowhead Airport (June 1 to June 8, 1976).

from the St. Louis area. Ozone concentration measurements during these days exhibited high maximums during the day, with 10 and 11 hours over the NAAQS, respectively, and low minimums at night. During the afternoon of June 7, the wind direction shifted to a westerly flow, and a minimum ozone concentration of 50 $\mu g/m^3$ was maintained overnight. Wind flow was from a westerly direction on the morning of the launch. The wind direction and behavior of ozone both confirmed that on the morning of June 8, 1976, the DaVinci II balloon was launched into back-ground air coming from a rural-type suburban area.

During the flight of the DaVinci II balloon, the instrumentation aboard the RTI-EML measured and recorded air quality data along and underneath the balloon flight track. Ozone, NO, NO_x, SO_2, THC, CH_4, CO, temperature and dew point data and bus speed were measured and recorded. Since the objective was to maintain visual contact and stay as nearly as possible underneath the balloon, the RTI-EML had to make frequent stops to await the balloon to catch up, especially during the time when the balloon floated around the city. A detailed log (written and tape recorded) was maintained to document the position, time, and status of the RTI-EML. Air quality data obtained during the flight are tabulated in appendix B.

Data collected on board the RTI-EML along the flight track shown in figures 6 and 7 were tabulated and validated. Selected ozone data were then utilized to first prepare 15-minute averages and then hourly average values for comparison to ozone measurements on board the DaVinci II balloon. Hourly average ozone measurements obtained as described above and 5-minute ozone concentrations measured on board the balloon on the hour are plotted in figure 10. Ozone concentrations measured at flight altitude ($\approx$ 800 m) remained in the range of 230-290 $\mu g/m^3$ from 1700 on the evening of June 8 until the gondola monitor was turned off at 0700 the next morning, with the exception of the time interval between 2141 and 2310 on June 8. The ozone concentration measured at flight level at 2219 decreased significantly to 122 $\mu g/m^3$. The drop in ozone concentration coincided with an observation made by the flight crew of a pungent hydrocarbon odor. The measured ozone concentration at 2310 was 240 $\mu g/m^3$. The location of the balloon at 2219 was 30 km downwind of a refining and 50 km downwind of a power plant. These measurements

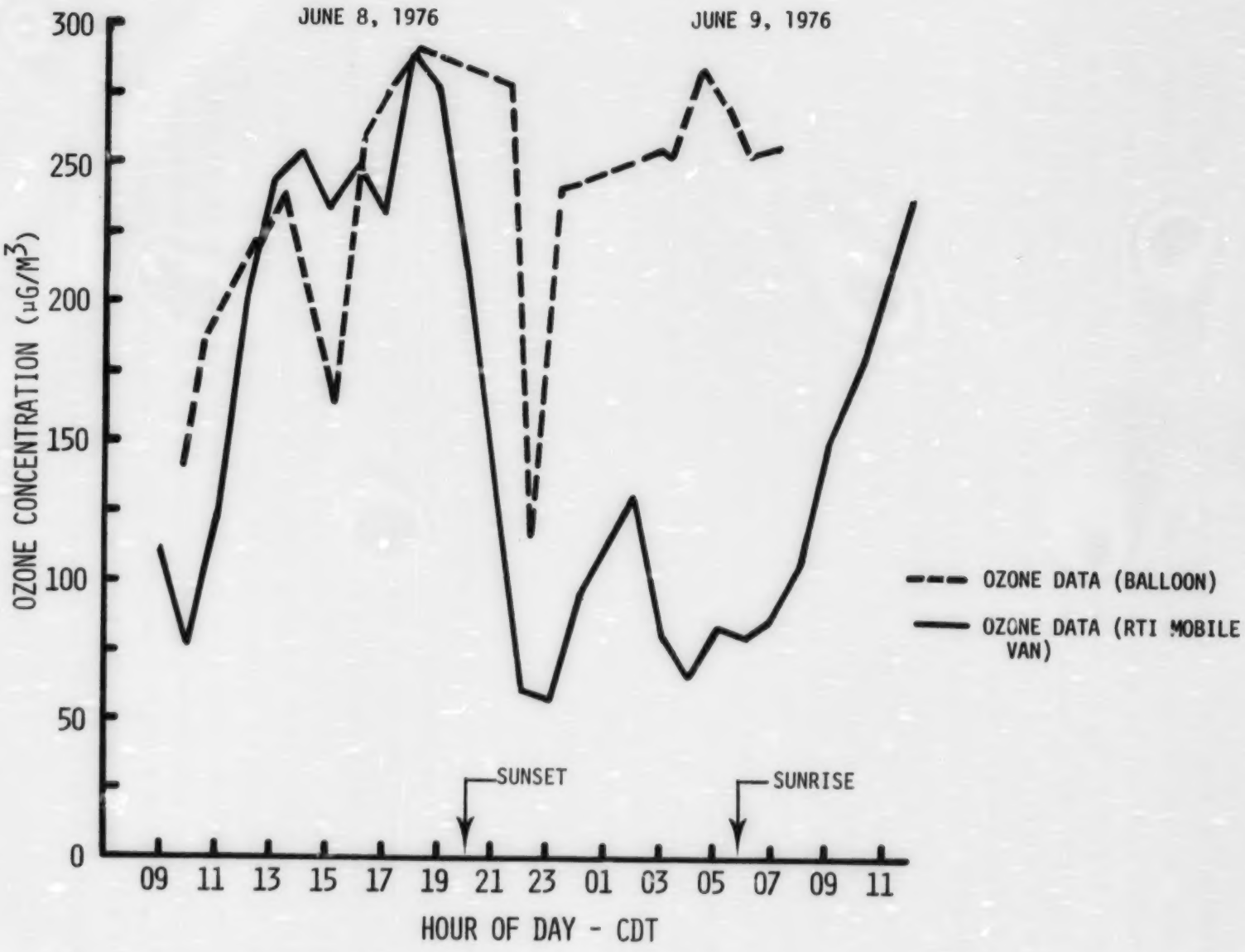

Figure 10. Airborne and ground-level ozone concentrations during the flight of DaVinci II (June 8-9, 1976).

strongly suggest transport aloft with minimum dilution and/or destruction (i.e., less than 20 percent during the nighttime regime).

The ozone concentrations at the ground show a rapid decrease with nightfall to a minimum of approximately 60 $\mu g/m^3$. Judging from the balloon track at 800 m altitude, and the wind pattern at the ground and at 1500 m, a windspeed and wind directional shear with altitude are indicated during the nocturnal phase of the flight. The temperature data strongly indicate that a well-developed radiation inversion formed and persisted through the night. The presence of the high pressure system suggests a subsidence inversion existed at an altitude above the balloon. The strong radiative inversion would tend to separate the flow aloft from flow at the ground as well as permit destruction of ozone in the low levels during the night without permitting downward diffusion from aloft.

Precursor concentrations (hydrocarbons and oxides of nitrogen) measured at ground level on board the RTI-EML are tabulated in appendix B. Results of selected hydrocarbon and halocarbon analyses of grab samples collected on board the DaVinci II balloon are tabulated in appendix C. These results are presented in chronological order by time as they were collected. Concentrations of selected compounds were plotted versus time and are shown in figures 11 and 12.

Figure 11 is a histogram plot of acetylene, isopentane, and Freon 11 concentrations for these grab samples. Acetylene, isopentane, and Freon 11 were selected because they are anthropogenic pollutants emitted primarily from automobiles or industrial processes or activities. Figure 12 is a histogram plot of methane and carbon monoxide concentrations in grab samples collected on board the DaVinci II balloon, as measured by the Beckman 6800 air quality analyzer and the summation concentration of the nonmethane hydrocarbons analyzed gas chromatographically. Nonmethane hydrocarbon concentrations are plotted in concentration units of parts per million carbon.

Three samples collected during the DaVinci II flight at an altitude of approximately 800 m had methane concentrations of 35.5, 112.6, and 36.6 ppm, respectively. Methane concentrations for the other grab samples averaged 1.6 ppm, which is very close to the geochemical background. Interestingly, the nonmethane hydrocarbon concentrations (Σ NMHC analyzed) for these three

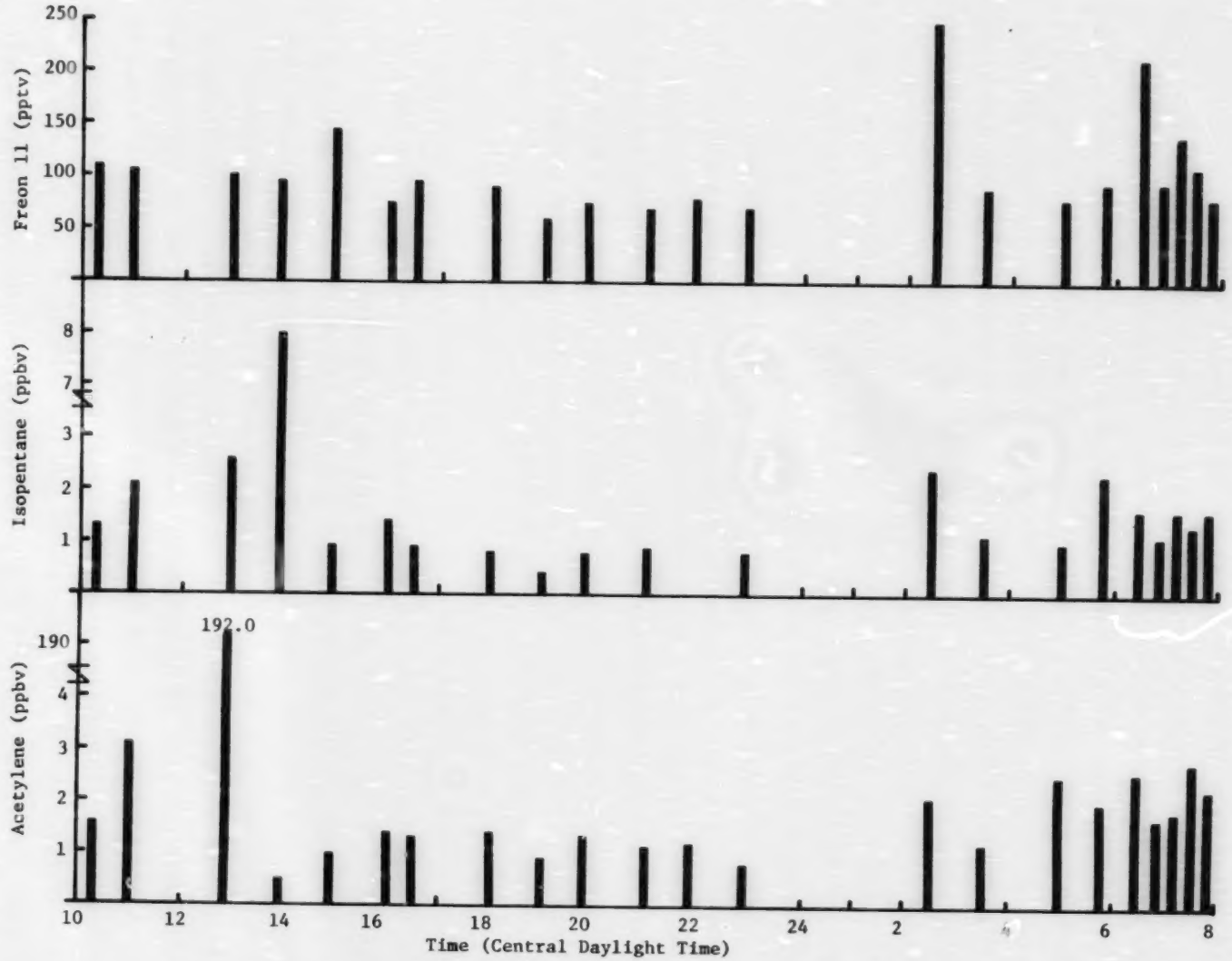

Figure 11. Histogram plot of acetylene, isopentane, and Freon 11 concentrations for samples collected onboard the DaVinci balloon.

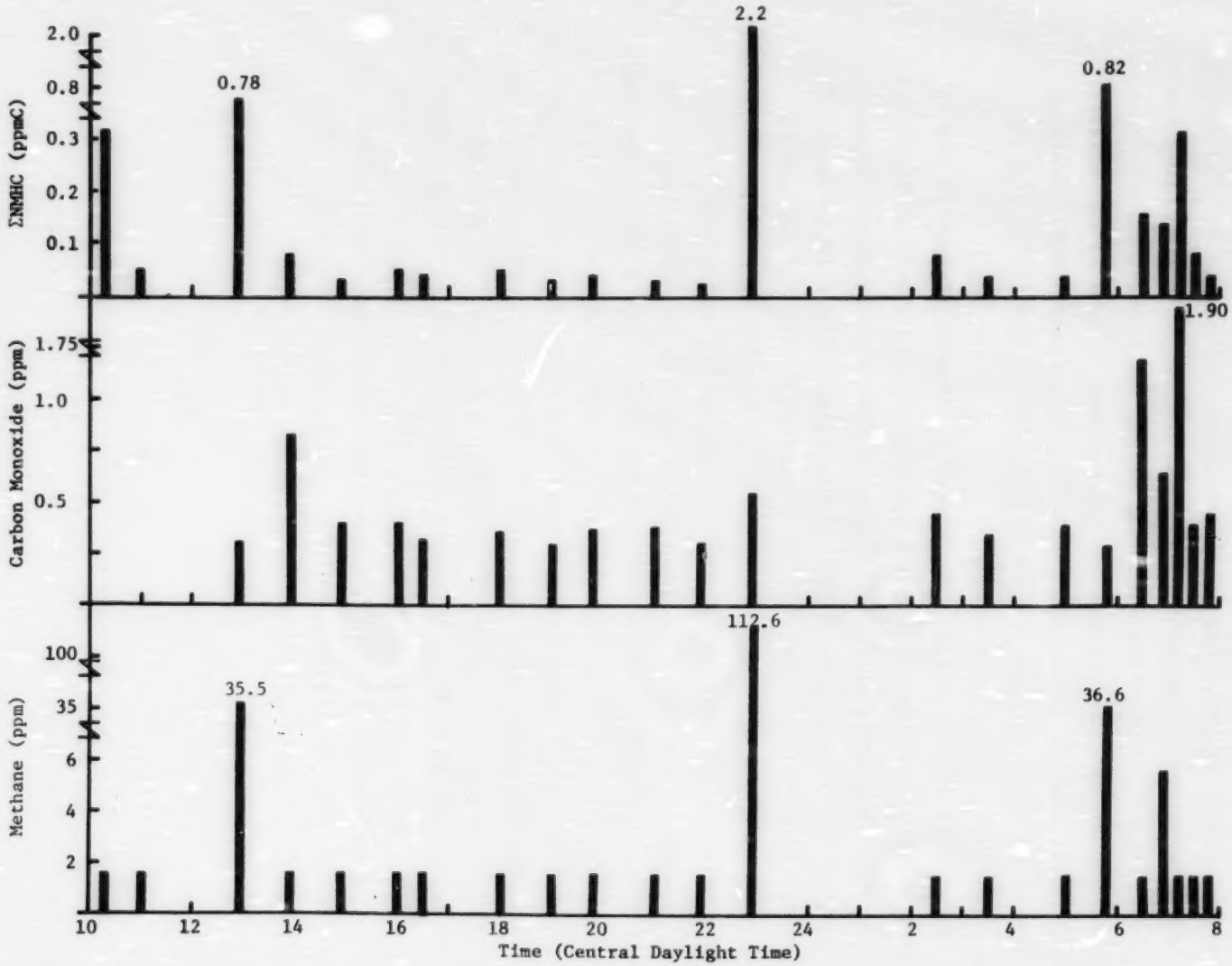

Figure 12. Histogram plot of total hydrocarbon, carbon monoxide, and Σ NMHC concentrations for samples collected onboard the DaVinci II balloon.

samples increased significantly. Carbon monoxide concentrations, however, did not increase. The acetylene concentration in the sample at 1344 (191.5 ppbv) was a factor of 6 higher than any other sample collected during the flight. Acetylene for the other two samples was low. Isopentane in that sample was higher than the average for all samples. Freon 11 was slightly higher than the average. The high total hydrocarbon and Σ NMHC concentrations for these three samples must be related to a point source such as a refinery or other industrial process.

The concentration of all six pollutants plotted in figures 11 and 12 were high in samples collected onboard the DaVinci II balloon as it floated above the St. Louis area, until approximately 1500-1600 in the afternoon. The location of the balloon at this time was approximately 30 km north of the downtown area. In general, the concentration of all six pollutants decreased or in the case of methane remained constant as the balloon drifted eastward until 2200, at which time methane and the Σ NMHC concentrations increased dramatically. The carbon monoxide concentration for this sample increased slightly. Grab samples were not collected during the time interval of 2200 on June 8 to 0200 on June 9. Acetylene, isopentane, and Freon 11 concentrations generally increased in samples collected from 0200 until the last sample was collected at 0745. Methane, carbon monoxide, and the Σ NMHC concentrations decreased in samples collected from 0220 until 0550, at which time the concentration of methane and the Σ NMHC increased by more than a factor of 10. The sample at 0700 also had a high concentration of all three components. The carbon monoxide concentration in the 0700 sample was the highest for any sample. Methane, carbon monoxide, and the Σ NMHC decreased in the remaining samples collected at flight level.

4.0 TENTATIVE CONCLUSIONS

The tentative conclusions presented in this report are based on preliminary examination of the ozone data collected aboard the balloon and ozone and precursor data collected aboard the RTI-EML during the flight of DaVinci II. A detailed analysis and evaluation of all data collected during the DaVinci II flight will be conducted in the near future under a separate contract. The tentative conclusions are as follows:

(1) General meteorological conditions--a subsidence inversion aloft and a strong radiative inversion based at the ground--were nearly ideal for long-distance transport aloft of ozone and ozone precursors at night, while keeping them separated from ground level emissions and destruction and limiting their vertical mixing.

(2) Ozone concentrations measured aloft above the radiation inversion remained in the range 230 to 290 $\mu g/m^3$ from 1700 on June 8 until the flight was ended the next day. These measurements strongly suggest overnight transport of ozone aloft with minimum dilution and/or destruction (i.e., < 20 percent).

(3) Ozone concentrations measured at the ground show a rapid decrease with nightfall to a minimum of about 60 $\mu g/m^3$.

(4) The occurrence of high ozone concentrations (> 250 $\mu g/m^3$) on the morning of June 9, 1976, in a rural area in southwestern Indiana was attributed to long-distance transport of ozone in an urban plume from St. Louis, Missouri. Long-distance transport is the most plausible explanation for the high ozone occurrence based on data available at this time.

(5) To successfully investigate the transport and transformation phenomena associated with large aerial urban plumes, it is necessary to optimize three methods of data measurement: ground stations, aircraft, and unmanned balloons. The aircraft measurements provide discrete time and spatial distribution measurements, which are essential in identifying boundary conditions for the plume. The balloon platform can provide a continuous time series

analysis of the chemical processes relevant to the physical stability characteristics of the parcel of air in question, and the fixed ground stations can perform as truth points for the calibration and control of the entire field measurement program. This type of a comprehensive data measurement program is unique for the air quality plume measurements and should provide considerable data for subsequent analysis and modeling.

5.0 REFERENCES

1. Research Triangle Institute, Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies, Environmental Protection Agency Report No. EPA-450/3-75-035, March 1975.
2. Research Triangle Institute, Study of the Formation of Ambient Oxidants in the Western Gulf Coast and North-Central and Northeast Regions of the United States, Environmental Protection Agency Report No. EPA-450/3-76-033, August 1976.

APPENDIX A

RTI AIR QUALITY DATA (MEASUREMENTS PRIOR TO DaVINCI II FLIGHT)

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PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 23, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temperatur (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
01										
02										
03										
04										
05										
06										
07										
08										
09										
10	1	19	67	1055	975	615	121	4	42°	16
11	0	14	83	997	962	899	55	4	60	19
12	0	13	108	989	927	748	60	5	48	20
13	0	7	138	977	977	634	32	6	52	22
14	0	4	163	957	957	600	24	5	77	23
15	0	6	168	972	947	564	63	4	89	23
16	0	9	171	982	926	434	99	5	68	24
17	0	8	161	977	977	477	74	7	46	23
18	0	5	141	932	923	432	19	7	44	22
19	0	3	128	975	975	382	14	7	31	21
20	0	8	99	978	972	398	48	7	29	19
21	0	5	88	965	965	309	15	6	33	18
22	0	7	83	960	960	457	9	5	37	17
23	0	8	77	958	933	557	34	4	27	16
24	0	6	82	1032	1029	432	27	4	28	16

T = Test or calibrate.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 24, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temperature (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
01	0	17	54	1039	1039	555	119	4	22	16
02	0	14	51	1010	999	359	81	5	29	16
03	0	17	42	985	953	483	94	5	24	15
04	0	30	17	950	920	513	229	6	20	14
05	0	29	23	965	965	433	202	6	21	13
06	0	12	37	950	950	392	81	4	23	11
07	0	16	30	945	934	376	113	5	24	11
08	5	31	22	T	T	T	183	6	20	12
09	9	37	25	T	T	T	208	6	20	12
10	12	41	37	T	T	T	218	4	62	14
11	2	27	65	T	T	T	126	4	34	16
12	C	C	90	T	T	T	T	4	33	18
13	2	[illegible]	141	T	T	T	79	5	59	20
14	3	23	136	T	T	T	166	5	29	21
15	1	7	166	1088	1039	450	49	6	3	22
16	1	5	169	1066	1022	406	26	6	16	22
17	1	4	169	1064	1024	461	18	5	21	22
18	1	3	156	1051	1038	452	3	5	25	22
19	0	3	149	1066	1017	368	4	5	24	21
20	0	8	122	1069	1020	952	29	4	2	20
21	1	13	100	1079	1041	1111	44	3	342	17
22	0	13	91	1085	1083	590	16	2	1	15
23	1	16	77	1143	1143	851	8	1	48	15
24	0	18	69	1286	1225	767	22	2	25	13

T = Test or calibrate.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 25, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temperature (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
01	0	20	72	1207	1207	910	79	5	45	14
02	2	24	57	1186	1110	1446	70	4	42	13
03	0	23	48	1347	1298	1161	75	2	35	11
04	1	21	55	1202	1160	979	44	2	7	9
05	1	14	50	1308	1172	1557	32	0	39	8
06	0	14	82	1278	1153	931	29	0	152	7
07	1	16	90	1237	1111	872	33	0	102	7
08	6	29	84	1169	1137	793	31	3	14	11
09	3	18	76	1108	1108	583	40	4	13	12
10	2	13	90	T	T	T	57	5	15	14
11	T	T	84	T	T	T	35	5	11	16
12	5	20	76	1115	1091	329	T	4	42	17
13	8	31	76	1096	1083	303	187	4	51	19
14	5	21	91	1109	1051	298	133	5	21	20
15	2	11	116	T	T	T	70	4	34	21
16	3	20	111	1076	1065	340	129	5	60	21
17	2	19	117	1060	1045	315	109	4	109	21
18	1	10	139	1060	1035	430	37	3	41	21
19	1	8	144	1074	1063	457	21	3	30	20
20	0	6	139	1076	1062	367	16	2	6	19
21	3	20	116	1122	1058	757	22	1	270	16
22	1	32	59	1268	1135	825	20	0	179	13
23	2	46	21	1356	1194	1091	31	0	215	12
24	2	30	32	1378	1214	838	22	0	215	12

T = Test or calibrate.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 26, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temperature (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
01	1	28	21	1351	1198	640	17	0	210	11
02	3	34	7	1359	1194	712	21	0	221	10
03	26	68	0	1641	1370	1145	34	1	108	9
04	28	66	0	1684	1439	1187	33	0	247	8
05	42	78	0	1748	1436	1213	34	0	173	7
06	70	117	0	1938	1558	1628	44	0	127	7
07	71	108	1	2045	1642	1648	42	0	125	7
08	47	92	13	T	T	T	T	0	151	11
09	62	132	T	2718	2250	2149	96	1	110	16
10	T	T	T	T	T	T	T	T	T	T
11	3	17	120	1153	1068	582	42	5	119	21
12	1	6	143	1096	1051	447	17	5	122	22
13	0	5	153	1084	1061	401	13	4	119	23
14	0	3	158	1074	1056	372	20	6	142	23
15	0	4	165	1080	1071	411	30	4	120	24
16	0	5	172	1083	1065	389	28	4	120	24
17	0	11	167	1101	1065	448	68	4	155	23
18	0	14	163	1072	1017	446	91	4	141	23
19	0	12	168	1093	1052	487	67	4	125	23
20	0	22	136	1132	1060	543	51	2	147	22
21	4	43	79	1236	1065	934	57	1	153	19
22	14	78	8	1343	1128	1487	59	0	82	16
23	24	92	1	1492	1212	1575	75	0	70	16
24	23	90	1	1808	1509	1601	77	0	41	16

T = Test or calibrate.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 27, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	15	87	2	1550	1270	1424	73	2	213	16	
02	0	22	70	1216	1104	592	37	2	232	16	
03	0	8	93	1124	1065	367	22	1	246	15	
04	0	6	88	1135	1067	360	19	1	221	14	
05	0	5	85	1111	1062	388	17	1	92	14	
06	0	7	62	1175	1089	456	14	0	61	14	
07	1	25	34	1740	1560	532	29	1	20	14	
08	14	59	19	1788	1625	979	49	2	31	16	
09	12	60	42	1424	1205	1356	91	3	96	18	
10	T	T	T	1385	1271	1350	96	5	106	20	
11	T	T	87	T	T	T	T	5	107	21	
12	2	22	99	T	T	T	42	4	98	22	
13	1	11	129	1089	1077	382	32	5	91	22	
14	0	9	139	1091	1074	413	32	4	78	22	
15	0	8	143	1081	1073	386	26	4	74	22	
16	0	12	129	1063	1047	437	23	4	41	22	
17	3	16	118	1109	1075	500	22	4	41	22	
18	0	16	111	1159	1126	439	31	3	22	20	
19	0	15	103	1099	1037	456	15	3	21	19	
20	0	28	74	1327	1297	555	26	2	42	17	
21	0	37	46	1322	1197	735	32	1	11	16	
22	0	25	50	1403	1299	529	32	0	5	16	
23	0	31	44	1262	1172	688	45	0	251	15	
24	2	33	26	1344	1116	746	38	0	242	15	

T = Test or calibrate.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 28, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	2	37	26	1317	1212	693	38	0	298	15	
02	1	27	54	1166	1108	501	45	1	345	15	
03	0	12	86	1059	1038	334	35	2	8	15	
04	0	6	105	1065	1065	347	19	3	30	15	
05	0	5	98	1070	1070	312	23	5	25	15	
06	0	5	101	1060	1049	311	35	5	20	15	
07	0	7	97	1047	1036	324	37	5	14	14	
08	0	11	84	1069	1026	533	28	4	9	15	
09	1	16	72	1087	1055	577	30	5	5	15	
10	1	9	84	1078	1057	416	20	4	1	15	
11	1	8	84	1066	1026	413	15	5	4	15	
12	T	T	T	T	T	T	T	T	T	T	T
13	T	T	T	T	T	T	T	T	T	T	T
14	1	6	92	1080	1063	391	50	4	1	16	14
15	1	8	91	1081	1055	402	55	3	3	17	14
16	1	4	105	1079	1053	402	33	3	358	17	14
17	1	4	105	1077	1040	492	36	3	355	18	14
18	2	14	92	1084	1063	489	78	3	335	18	14
19	1	3	110	1068	1052	439	24	2	348	18	14
20	1	7	92	1085	1048	498	26	1	339	18	15
21	1	7	86	1082	1055	436	29	1	331	17	15
22	1	6	64	1182	1119	540	18	0	271	16	14
23	1	12	43	1126	1097	502	20	1	242	16	14
24	1	11	46	1131	1093	477	22	0	259	16	15

T = Test or calibrate.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 29, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	2	14	40	1150	1079	493	24	0	237	16	14
02	2	18	22	1265	1102	502	29	1	218	14	13
03	1	11	18	1214	1098	543	13	0	253	13	12
04	3	13	7	1189	1136	563	14	2	216	13	12
05	2	5	20	1135	1100	417	11	1	219	13	12
06	0	4	20	1172	1114	449	10	0	150	12	11
07	1	4	19	1193	1135	471	5	1	214	13	12
08	2	2	28	1118	1082	435	8	1	234	13	13
09	3	2	44	1115	1088	405	7	1	246	15	14
10	2	1	69	1092	1065	390	25	1	264	18	15
11	2	1	98	1079	1049	383	52	1	226	21	16
12	2	5	130	1070	1048	432	89	1	132	23	16
13	2	4	160	1074	1023	545	88	2	165	24	15
14	T	T	T	T	T	T	T	2	127	26	13
15	2	11	232	T	T	T	T	2	171	26	14
16	1	8	229	1073	1039	464	91	3	189	26	15
17	2	8	216	1071	1044	493	125	4	162	26	15
18	2	10	219	1060	1030	484	121	5	146	26	14
19	1	15	188	1065	1043	463	86	5	137	25	14
20	1	14	171	1071	1030	503	52	5	165	24	15
21	1	15	144	1080	1043	539	52	5	163	22	16
22	1	16	117	1086	1057	500	55	4	148	21	16
23	1	24	86	1088	1043	548	93	3	147	20	16
24	2	19	79	1099	1064	509	86	0	190	19	16

T = Test or calibrate.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 30, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	1	13	79	1103	1061	546	66	2	290	19	17
02	2	12	57	1128	1083	561	43	1	177	19	17
03	1	15	92	1144	1046	456	33	M	M	M	M
04	1	5	142	1046	1013	250	21	M	M	M	M
05	1	11	111	1079	1013	285	35	M	M	M	M
06	1	2	130	1013	981	194	14	M	M	M	M
07	1	4	155	1046	981	342	20	M	M	M	M
08	2	5	97	1112	1046	285	37	M	M	M	M
09	1	7	82	1079	1013	273	31	M	M	M	M
10	1	15	76	1177	1046	342	30	M	M	M	M
11	1	7	113	1046	1013	285	37	M	M	M	M
12	2	T	113	1145	1074	425	T	2	161	20	17
13	1	11	129	T	T	T	97	M	M	M	M
14	2	7	141	T	T	T	83	1	258	23	18
15	1	5	154	T	T	T	73	M	M	M	M
16	1	4	145	1177	1046	228	46	M	M	M	M
17	0	5	147	1112	981	331	34	M	M	M	M
18	1	15	122	1112	981	342	101	M	M	M	M
19	1	9	122	1079	981	228	84	M	M	M	M
20	1	5	121	1079	981	171	44	M	M	M	M
21	1	9	97	1177	1046	285	30	M	M	M	M
22	1	15	61	1209	1046	570	26	M	M	M	M
23	4	61	10	1406	1145	1026	44	M	M	M	M
24	2	51	13	1308	1079	912	85	M	M	M	M

T = Test or calibrate. M = Missing data.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: May 31, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	1	15	80	1177	1013	456	59	M	M	M	M
02	1	13	56	1177	1046	456	65	M	M	M	M
03	1	12	58	1177	1014	513	55	M	M	M	M
04	1	9	58	1177	1046	342	55	M	M	M	M
05	1	5	69	1144	1046	342	44	M	M	M	M
06	1	4	53	1144	981	285	34	M	M	M	M
07	1	4	66	1177	1046	285	34	M	M	M	M
08	2	4	65	1144	1013	342	33	M	M	M	M
09	1	10	70	1243	1079	400	54	M	M	M	M
10	1	11	76	1144	1046	399	97	M	M	M	M
11	1	10	97	1144	981	285	98	M	M	M	M
12	2	16	103	1111	1013	228	262	M	M	M	M
13	1	6	121	1079	981	365	197	M	M	M	M
14	1	4	132	IF	IF	IF	46	M	M	M	M
15	T	T	132	IF	IF	IF	T	M	M	M	M
16	1	12	125	IF	IF	IF	65	M	M	M	M
17	1	10	123	IF	IF	IF	68	M	M	M	M
18	2	33	92	IF	IF	IF	67	M	M	M	M
19	1	32	98	IF	IF	IF	69	M	M	M	M
20	1	31	84	IF	IF	IF	78	M	M	M	M
21	1	20	66	IF	IF	IF	44	M	M	M	M
22	1	18	51	IF	IF	IF	31	M	M	M	M
23	1	18	37	IF	IF	IF	22	M	M	M	M
24	1	18	34	IF	IF	IF	14	M	M	M	M

IF = Instrument failure. M = Missing data (computer failure).

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: June 1, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	1	20	23	IF	IF	IF	16	M	M	M	M
02	1	18	30	IF	IF	IF	16	M	M	M	M
03	1	10	55	IF	IF	IF	7	M	M	M	M
04	1	1	70	IF	IF	IF	5	M	M	M	M
05	1	1	88	IF	IF	IF	12	M	M	M	M
06	1	1	93	IF	IF	IF	16	M	M	M	M
07	1	5	78	IF	IF	IF	13	M	M	M	M
08	1	11	82	IF	IF	IF	17	M	M	M	M
09	1	5	119	IF	IF	IF	18	M	M	M	M
10	1	T	131	T	T	T	21	M	M	M	M
11	1	4	159	1193	1128	687	14	1	281	21	16
12	0	3	175	1168	1131	580	14	1	229	22	16
13	0	2	180	1133	1102	491	10	3	229	24	15
14	0	1	184	1117	1100	390	7	4	30	24	15
15	2	14	162	1133	1113	378	66	5	23	25	14
16	2	21	152	1141	1102	478	102	4	43	25	14
17	0	11	189	1150	1123	521	23	4	43	25	15
18	1	13	209	1155	1105	593	47	4	46	25	15
19	0	10	188	1131	1092	450	42	4	38	24	15
20	T	T	T	1186	1106	421	T	4	37	23	15
21	1	11	159	T	T	T	29	2	53	21	15
22	1	20	104	1191	1130	604	30	1	151	19	15
23	1	31	52	1275	1165	920	44	0	142	18	15
24	1	54	14	1598	1420	1183	67	1	227	18	15

T = Test or calibrate. M = Missing data (computer failure).

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: June 2, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	1	52	2	1714	1487	1386	71	1	26	18	15
02	2	48	13	1734	1525	1282	68	2	347	17	15
03	1	10	81	1205	1147	616	57	4	22	18	15
04	1	5	93	1162	1118	662	36	3	17	17	14
05	1	4	96	1138	1124	614	27	3	5	17	14
06	1	4	90	IF	IF	IF	42	M	M	M	M
07	1	4	81	IF	IF	IF	29	M	M	M	M
08	1	6	66	IF	IF	IF	26	M	M	M	M
09	1	11	57	IF	IF	IF	46	M	M	M	M
10	2	13	59	IF	IF	IF	52	M	M	M	M
11	2	27	61	IF	IF	IF	124	M	M	M	M
12	2	31	79	IF	IF	IF	137	M	M	M	M
13	2	26	121	IF	IF	IF	137	M	M	M	M
14	1	6	154	IF	IF	IF	48	M	M	M	M
15	2	18	141	IF	IF	IF	124	M	M	M	M
16	1	9	170	IF	IF	IF	72	M	M	M	M
17	1	1	171	IF	IF	IF	26	M	M	M	M
18	1	5	169	T	T	T	59	M	M	M	M
19	T	T	T	1030	968	298	T	7	16	24	9
20	1	5	150	1027	1013	325	16	4	15	23	10
21	0	13	124	1068	1013	547	20	2	360	20	11
22	0	15	97	1127	1063	574	25	1	26	19	12
23	0	19	75	1187	1114	469	19	2	40	18	12
24	0	19	64	1334	1267	419	32	2	13	16	12

T = Test or calibrate. IF = Instrument failure. M = Missing data (computer failure).

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: June 3, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	0	23	73	1156	1085	427	70	2	29	16	11
02	0	16	82	1433	1318	475	28	3	15	15	11
03	0	6	104	1353	1301	334	12	3	20	14	9
04	0	5	98	1275	1236	305	21	3	7	13	8
05	0	10	69	1154	1075	312	26	2	11	12	8
06	0	9	57	1160	1063	334	19	1	8	12	8
07	0	10	49	M	M	M	20	M	M	M	M
08	0	12	65	M	M	M	50	M	M	M	M
09	0	47	44	1183	1069	451	203	4	27	16	7
10	0	55	51	IF	IF	IF	245	4	16	18	9
11	0	14	114	IF	IF	IF	55	4	11	20	9
12	0	12	143	IF	IF	IF	70	6	23	22	9
13	0	10	167	IF	IF	IF	67	6	18	23	10
14	0	10	170	IF	IF	IF	68	6	29	24	10
15	0	17	162	IF	IF	IF	126	7	32	25	10
16	0	11	179	IF	IF	IF	94	6	28	24	10
17	T	T	T	T	T	T	T	5	16	24	10
18	13	9	158	1095	1063	440	T	4	19	23	10
19	10	11	141	1140	1135	403	45	3	20	23	10
20	9	11	139	1074	1057	478	35	3	2	22	10
21	9	14	126	1082	1064	561	28	2	345	21	10
22	9	16	92	1097	1080	540	23	2	19	19	11
23	8	17	79	1127	1090	603	16	2	35	19	11
24	8	12	82	1122	1114	388	13	1	20	19	11

T = Test or calibrate. IF = Instrument failure. M = Missing data (computer failure).

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: June 4, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	8	10	84	1124	1115	420	11	2	32	19	11
02	8	12	93	1494	1466	461	24	3	46	19	11
03	8	8	108	1273	1233	416	34	2	27	19	12
04	8	6	103	1361	1331	422	22	3	22	19	11
05	8	6	104	1334	1334	376	26	3	30	19	11
06	8	7	102	1297	1213	462	37	3	22	19	11
07	8	11	90	IF	IF	IF	46	M	M	19	11
08	8	11	78	IF	IF	IF	60	M	M	19	11
09	8	11	75	IF	IF	IF	55	M	M	19	11
10	8	23	74	IF	IF	IF	107	M	M	19	11
11	10	18	86	IF	1113	709	94	4	71	20	14
12	10	15	92	1255	1138	674	65	4	72	21	15
13	T	T	101	T	T	T	T	8	67	21	15
14	3	12	121	1147	1031	691	41	5	58	23	16
15	2	10	145	1149	1100	584	45	4	87	24	16
16	2	12	152	1153	1083	637	40	4	100	24	16
17	2	10	163	1125	1073	608	33	4	90	25	16
18	2	15	141	1197	1101	651	42	4	81	24	16
19	3	21	138	1158	1187	891	54	4	73	24	17
20	2	14	146	IF	IF	IF	48	3	80	23	16
21	1	20	121	IF	IF	IF	49	2	80	22	16
22	2	25	89	IF	IF	IF	56	2	60	20	16
23	2	34	44	IF	IF	IF	57	0	69	19	16
24	14	71	7	IF	IF	IF	65	1	78	18	16

T = Test or calibrate. IF = Instrument failure. M = Missing data (computer failure).

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: June 5, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	17	43	71	IF	IF	IF	43	3	135	18	16
02	1	11	95	IF	IF	IF	26	1	89	17	16
03	2	13	66	IF	IF	IF	24	0	330	17	16
04	3	27	28	IF	IF	IF	28	0	176	17	15
05	10	41	10	IF	IF	IF	41	2	35	18	16
06	2	16	39	IF	IF	IF	43	1	33	18	17
07	3	17	28	IF	IF	IF	31	1	22	19	17
08	5	21	40	IF	IF	IF	50	2	56	20	17
09	6	24	65	IF	IF	IF	78	2	86	21	17
10	6	27	78	IF	IF	IF	113	3	105	22	18
11	6	28	86	IF	IF	IF	159	3	110	23	17
12	T	T	120	IF	IF	IF	T	4	117	24	17
13	3	14	156	IF	IF	IF	37	4	115	24	17
14	3	9	169	IF	IF	IF	30	5	112	26	16
15	2	9	178	IF	IF	IF	34	5	120	26	17
16	2	6	170	IF	IF	IF	32	5	126	26	17
17	2	6	146	IF	IF	IF	25	5	122	26	17
18	2	5	135	IF	IF	IF	23	4	111	25	16
19	2	5	137	IF	IF	IF	19	4	124	25	16
20	2	9	115	T	T	T	14	3	117	24	15
21	1	14	97	1129	1016	284	16	3	124	23	15
22	3	25	58	1230	1075	380	28	1	120	21	15
23	4	28	18	1285	1090	575	27	0	58	19	16
24	7	35	15	1479	1320	576	25	0	72	19	15

T = Test or calibrate. IF = Instrument failure.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: June 6, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	29	79	1	1629	1332	1093	42	0	114	17	15
02	34	93	1	1572	1265	1144	91	2	111	17	13
03	26	76	1	1606	1312	1018	92	1	69	16	11
04	7	58	16	1817	1525	972	90	0	335	16	11
05	6	52	17	1677	1418	883	80	0	113	14	10
06	6	37	23	1688	1456	756	69	0	138	13	10
07	16	49	15	1692	1410	888	66	0	115	14	12
08	10	31	48	1692	1455	675	53	0	71	17	13
09	7	24	96	T	T	T	82	1	77	20	11
10	3	20	135	T	T	T	62	2	123	22	10
11	2	11	181	1189	1114	536	89	2	90	24	9
12	1	8	215	1196	1107	498	44	3	72	25	7
13	1	9	213	1193	1062	564	40	3	110	25	7
14	1	6	223	1146	1071	493	41	3	84	26	7
15	0	6	293	IF	1064	508	31	3	102	26	8
16	1	7	245	IF	1066	589	22	3	94	27	8
17	1	6	252	IF	1081	628	23	2	106	27	8
18	0	6	253	IF	1080	630	27	3	80	26	7
19	0	8	245	IF	1080	631	28	2	43	26	7
20	0	11	212	IF	1079	632	24	2	51	24	9
21	0	18	153	IF	1079	634	26	1	168	21	10
22	1	30	109	IF	1079	635	25	0	208	20	10
23	1	61	46	IF	1209	901	38	0	130	18	11
24	2	45	42	1460	1265	1288	35	1	213	16	12

T = Test or calibrate. IF = Instrument failure.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: June 7, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	2	27	42	1361	1228	894	29	0	229	15	12
02	8	46	5	1450	1232	1299	29	1	219	15	12
03	10	50	2	1362	1170	1041	27	2	216	14	11
04	5	26	32	1380	1148	978	27	1	210	14	11
05	3	14	40	1331	1127	724	20	0	208	13	10
06	20	44	8	IF	1276	1124	25	0	138	12	10
07	27	44	13	IF	1299	1982	27	0	185	13	11
08	4	10	46	IF	1248	1280	24	1	209	15	14
09	3	11	83	1556	1247	1283	23	1	212	18	14
10	2	9	106	T	T	T	T	1	301	22	13
11	2	7	187	1269	962	1107	57	1	199	25	12
12	2	19	204	1085	1051	568	56	2	131	26	11
13	1	17	239	1033	974	601	48	2	129	26	11
14	1	14	369	997	933	514	54	3	188	27	12
15	0	11	271	999	928	490	70	3	176	27	12
16	1	11	276	980	896	497	83	3	197	28	12
17	1	11	256	987	916	588	99	M	M	M	M
18	5	13	233	953	953	517	119	2	164	27	11
19	3	15	229	968	897	488	141	2	178	27	12
20	2	15	213	1011	907	721	128	1	204	26	13
21	2	19	178	1166	1020	865	134	0	238	22	14
22	2	32	107	1116	933	834	110	0	214	20	14
23	2	14	121	1139	1017	647	89	1	195	19	14
24	2	14	121	1139	1017	647	89	M	M	M	M

T = Test or calibrate. M = Missing data.

PROJECT DaVINCI II: AIR QUALITY DATA

Location: Arrowhead Airport

Date: June 8, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							WS (m/sec)	WD (°)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2				
01	M	M	M	M	M	M	M	M	M	M	M
02	1	16	78	1290	925	983	60	0	208	16	13
03	1	13	73	1136	1098	727	34	1	219	16	13
04	1	10	64	1139	997	674	27	1	209	15	13
05	4	18	52	1135	906	653	28	0	194	14	12
06	2	9	63	1095	961	647	20	1	206	14	12
07	T	T	T	T	T	T	T	T	T	T	T
08	2	8	122	3001	2937	5596	29	N.D.	N.D.	20	15
BALLOON LAUNCH @ 0857				RTI VAN DEPARTED @ 0902							

T = Test or calibrate. M = Missing data. N.D. = No data.

APPENDIX B

RTI AIR QUALITY DATA (INTRANSIT MEASUREMENTS DURING DaVinci II FLIGHT)

Project DaVinci II: Intransit Measurements

Date: June 8, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							Bus Speed (mph)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
0900	T	T	T	T	T	T	T	0	T	T
0915	423	—	145	1052	1023	479	38	8	22	14
0930	249	328	21	1648	946	386	118	58	23	14
0945	354	820	62	1225	1018	402	90	49	24	14
1000	360	588	76	1359	935	1198	316	9	26	12
1015	464	—	103	1187	965	1521	134	25	26	14
1030	1504	—	169	983	948	571	66	21	25	14
1045	88	—	190	1127	971	2406	165	0	26	13
1100	25	—	172	996	960	429	86	0	27	13
1115	64	—	225	996	944	1277	104	13	26	12
1130	864	1148	6	1227	946	1538	484	0	29	12
1145	80	160	205	1192	959	1091	301	15	28	13
1200	31	—	271	3049	978	986	221	23	27	12
1215	472	620	25	7433	1042	831	391	0	29	10
1230	82	148	237	1062	1015	522	163	38	28	12
1245	229	253	222	1572	945	1880	210	24	28	13
1300	50	—	304	1216	928	1878	110	26	28	13
1315	74	83	267	1027	916	473	106	14	28	13
1330	T	T	T	T	T	T	T	0	T	T
1345	170	270	191	941	899	481	127	14	27	12
1400	32	88	177	1134	918	1636	230	45	28	13
1415	4	20	294	1288	853	1136	141	0	28	12
1430	8	20	290	—	—	—	153	0	29	11
1445	531	652	172	—	—	—	155	0	29	12

T = Test. — = Missing data or measurement problem.

Project DaVinci II: Intransit Measurements

Date: June 8, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							Bus Speed (mph)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
1500	68	68	225	—	—	—	183	0	29	13
1515	12	20	269	—	—	—	96	0	29	13
1530	20	20	253	—	—	—	99	0	29	12
1545	60	102	230	—	—	—	123	36	29	12
1600	0	1	288	—	—	—	165	0	30	11
1615	5	23	120	—	—	—	126	0	29	11
1630	0	22	249	—	—	—	199	0	30	12
1645	24	35	266	—	—	—	192	33	28	12
1700	21	36	262	1017	917	233	116	0	30	11
1715	24	—	294	1002	972	133	114	11	29	12
1730	0	8	313	1001	916	124	—	0	28	14
1745	0	10	291	986	948	193	41	0	28	14
1800	0	15	268	972	928	197	28	0	28	13
1815	5	5	274	972	943	211	45	0	28	12
1830	2	8	282	964	939	257	34	0	28	12
1845	3	5	270	968	957	256	60	0	28	11
1900	34	69	120	979	951	444	82	0	28	12
1915	37	—	230	1142	950	432	69	32	27	14
1930	1	7	208	1063	1063	222	43	0	27	15
1945	11	11	201	1021	1002	336	31	29	26	14
2000	152	233	99	982	979	983	84	33	26	15
2015	67	93	166	—	—	—	157	14	26	15
2030	13	71	141	1301	1063	786	118	0	26	14
2045	52	90	107	1466	1140	1682	290	0	26	13

— = Missing data or measurement problem.

Project DaVinci II: Intransit Measurements

Date: June 8-9, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							Bus Speed (mph)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
2100	95	188	35	1308	1103	2188	216	31	26	12
2115*	42	64	148	1445	1051	3876	328	0	26	13
2130*	148	224	8	1862	1056	1214	384	0	24	16
2145	35	43	85	1575	1150	1987	493	16	23	15
2200	27	54	18	1250	1069	980	87	29	20	15
2215	55	84	96	1201	1107	646	164	27	23	15
2230*	20	60	98	3574	1247	31092	561	0	24	12
2245*	63	94	81	8011	1137	31092	912	31	24	13
2300	22	31	95	1211	1054	1305	133	19	20	14
2315	32	78	57	1176	1010	908	127	13	20	15
2330*	20	60	98	3574	1247	31099	561	0	24	12
2345	35	35	129	1223	1030	—	340	24	21	14
0000	6	12	99	1242	1007	2929	278	47	20	13
0015	35	52	62	1153	968	1315	126	53	18	13
0030	38	—	125	991	868	1990	108	48	19	13
0045	36	52	161	1457	942	1371	260	0	20	13
0100	18	20	206	—	1277	208	94	38	20	13
0115	37	48	102	2094	913	2024	92	43	18	13
0130	15	18	87	1082	1099	1416	93	30	19	12
0145	38	45	170	1006	1004	1419	84	31	20	15
0200	27	27	101	1120	980	679	83	33	18	14
0215	15	33	60	1116	1144	651	62	40	17	11
0230	18	37	71	1088	1059	527	270	26	19	13
0245	48	49	70	1657	1020	514	201	25	19	13

* = Suspected contamination of sample by generator exhaust.

— = Missing data or measurement problem.

Project DaVinci II: Intransit Measurements

Date: June 9, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							Bus Speed (mph)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
0300	16	16	64	1184	1125	484	39	0	16	15
0315	116	—	105	1415	1174	556	90	0	18	15
0330	18	19	70	1829	1498	560	77	45	17	14
0345*	43	—	49	1069	1069	2030	57	53	17	14
0400*	39	49	84	1259	1148	1226	94	43	17	12
0415*	366	462	7	1400	994	1990	138	56	16	12
0430*	35	47	47	1772	1071	2100	174	26	17	12
0445*	159	218	35	1236	1002	2269	0	41	16	13
0500*	26	—	82	1031	952	1322	59	0	16	13
0515*	108	142	39	3369	1083	393	147	16	16	13
0530*	47	52	77	1402	1129	641	—	11	16	13
0545*	148	158	39	1043	1029	447	157	7	17	13
0600	18	29	104	1095	1095	996	68	59	18	14
0615*	88	120	7	1151	1060	787	345	0	19	13
0630	33	—	68	1277	1162	665	94	51	19	15
0645	132	—	88	1272	1028	746	76	29	19	16
0700	31	—	85	1282	1262	2735	101	49	19	16
0715*	105	146	44	1399	1127	19191	104	47	20	15
0730	20	—	115	1162	1065	345	81	0	20	15
0745	26	—	120	1253	1060	479	122	55	20	15
0800	16	—	132	1219	1013	549	188	0	21	14
0815	31	43	86	1070	983	522	274	0	22	13
0830	5	—	205	992	869	399	136	48	23	14
0845*	30	—	171	1646	965	819	169	27	23	14

* = Suspected contamination of sample by generator exhaust.
— = Missing data or measurement problem.

Project DaVinci II: Intransit Measurements

Date: June 9, 1976

Time: Central Daylight Time

Time Hour	Concentration ($\mu g/m^3$)							Bus Speed (mph)	Temp (°C)	Dew Point (°C)
	NO	NO_x	O_3	THC	CH_4	CO	SO_2			
0900	35	35	160	1265	1006	1387	101	38	23	15
0915*	137	—	181	1203	984	1287	150	9	24	14
0930*	79	134	125	2669	1174	8296	833	0	25	14
0945*	78	179	96	2707	1027	1881	296	0	26	14
1000*	86	182	161	2784	1302	4665	329	0	27	14

* = Suspected contamination of sample by generator exhaust. — = Missing data or measurement problem.

APPENDIX C

HYDROCARBON AND HALOCARBON ANALYSIS RESULTS FOR
GRAB SAMPLES COLLECTED ABOARD DaVINCI II

HYDROCARBON AND HALOCARBON ANALYSIS RESULTS FOR GRAB SAMPLES
COLLECTED ABOARD DaVINCI II

JUNE 8, 1976

COMPOUND/TIME (CDT)	1019	1054	1245	1344	1452	1603	1638	1759	1859	1957	2103	2150	2258
Ethane and Ethylene*	158.4	13.9	340.6	16.8	8.8	13.9	9.9	17.6	9.4	12.4	9.2	8.2	1095.0
Propane*	28.3	3.7	8.6	3.4	2.9	3.5	3.6	3.9	3.2	3.6	4.4	2.5	1016.0
Propylene*	19.3	1.8	14.0	3.0	1.5	8.8	1.5	2.5	3.5	2.4	2.5	0.8	3.4
Acetylene*	3.1	6.1	383.0	0.9	1.9	2.8	2.4	2.9	1.9	2.7	2.2	2.3	1.3
Isobutane*	1.6	3.1	12.6	1.1	2.0	2.4	2.4	2.0	1.6	1.9	1.1	1.5	45.7
n-Butane*	62.0	11.8	2.9	8.6	6.7	10.4	7.0	8.0	6.4	6.7	5.8	5.0	6.3
1-Butene*	40.8	0.4	7.5	1.8	ND	ND	3.2	0.6	1.5	5.4	0.7	1.2	0.8
Trans-2-Butene*	2.0	ND	ND	ND	ND	ND	ND	ND	0.9	2.0	ND	ND	ND
Iscpentane*	7.0	10.7	11.2	39.8	4.8	7.3	4.4	4.3	1.8	3.0	3.3	ND	4.0
Cyclopentane*	ND	1.5	1.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Σ NMHC*	322.5	53.0	782.1	75.4	28.6	49.1	34.4	41.8	30.2	40.1	29.2	21.5	2172.5
CH_4 (ppm)	1.55	ND	35.5	1.52	1.53	1.55	1.52	1.52	1.55	1.52	1.52	1.55	112.6
CO (ppm)	1.86	ND	0.35	0.88	0.40	0.39	0.32	0.34	0.30	0.37	0.37	0.31	0.5
Freon 11**	113.0	106.0	101.0	98.0	141.0	87.0	99.0	91.0	66.0	75.0	71.0	82.0	73.0
Freon 12**	200.0	296.0	320.0	242.0	403.0	ND	372.0	439.0	245.0	315.0	227.0	201.0	275.0

* ppbc = Parts per billion carbon.

** pptv = Parts per trillion by volume.

Σ NMHC = Summation of the ten nonmethane hydrocarbons analyzed gas chromatographically.

ND = Not detected.

HYDROCARBON AND HALOCARBON ANALYSIS RESULTS FOR GRAB SAMPLES
COLLECTED ABOARD DaVINCI II

JUNE 9, 1976

COMPOUND/TIME (CDT)	0226	0335	0501	0541	0635	0656	0703	0724	0739				
Ethane and Ethylene*	16.8	7.3	9.8	388.0	61.0	63.8	150.0	32.4	9.4				
Propane*	10.5	3.4	4.4	369.0	20.9	40.0	32.6	5.5	3.8				
Propylene*	1.3	3.4	2.5	2.7	10.2	2.9	13.7	4.2	1.5				
Acetylene*	4.1	2.4	4.8	4.0	5.2	3.3	3.6	5.4	4.4				
Isobutane*	8.8	2.5	3.1	17.7	3.8	5.1	3.9	3.8	3.7				
n-Butane*	20.6	7.9	10.1	12.1	39.2	21.8	65.2	10.6	10.8				
1-Butene*	2.8	ND	1.7	0.5	12.8	4.8	34.6	3.7	0.5				
Trans-2-Butene*	ND	ND	ND	ND	3.9	0.6	8.4	5.9	ND				
Isopentane*	12.2	5.7	5.1	11.3	7.8	5.4	8.3	6.5	8.1				
Cyclopentane*	ND	ND	ND	ND	ND	ND	ND	ND	ND				
Σ NMHC*	77.1	32.6	41.5	805.3	164.8	147.7	320.3	77.6	42.2				
CH_4 (ppm)	1.52	1.46	1.53	36.6	1.55	5.61	1.53	1.49	1.53				
CO (ppm)	0.43	0.36	0.41	0.30	1.21	0.58	1.86	0.41	0.43				
Freon 11**	247.0	95.0	88.0	96.0	209.0	95.0	143.0	106.0	79.2				
Freon 12**	288.0	315.0	308.0	334.0	366.0	391.0	369.0	335.0	335.0				

*ppbc = Parts per billion carbon.

**pptv = Parts per trillion by volume.

Σ NMHC = Summation of the ten nonmethane hydrocarbons analyzed gas chromatographically.

ND = Not detected.

APPENDIX D

QUALITY CONTROL PROGRAM FOR HYDROCARBON SAMPLING

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APPENDIX D. QUALITY CONTROL PROGRAM FOR HYDROCARBON SAMPLING

A quality control program was implemented to determine whether (if) air samples collected in Tedlar bags for subsequent C_2-C_5 hydrocarbon analysis would experience significant contamination from the bag material or constituent loss (by wall permeation or sorption). The sampling protocol for the program was as follows: (1) all Tedlar bags were purged with hydrocarbon-free air prior to installation on the DaVinci II gondola; (2) Tedlar bags were protected from sunlight by an aluminized material (Scotchpack); (3) samples were stored after collection in air-tight aluminum suitcases and transported to RTI in the RTI-Environmental Monitoring Laboratory (RTI-EML); (4) the mean time between sample collection and analysis was 8 days; and (5) samples were analyzed in random order as they came from the shipping containers.

The quality control program consisted of sets of experiments to determine the potential for contamination of zero air by the Tedlar film and concentration losses due to sorption or permeation for hydrocarbon mixtures stored in Tedlar bags. These tests and results are described in the following paragraphs.

Zero air was analyzed directly from a cylinder purchased from Scott Environmental and then introduced into a Tedlar bag (Q.C.1). Q.C.1 was analyzed immediately and then shipped to St. Louis in the RTI-EML. Q.C.2 and Q.C.3 were filled using the same zero air cylinder at the field site on May 20 and June 7. Q.C. bags were returned to RTI and analyzed gas chromatographically. Results of this study, including the dates of preparation and analysis, are presented in Table D-1.

The results in Table D-1 indicate that contamination of zero air from hydrocarbon permeation from the outside and from the Tedlar film itself was insignificant and suggest that hydrocarbon contamination of ambient air samples should also be similar. Contamination due to halocarbons such as Freon 11 and 12 was also considered minimal; however, the data show serious problems with the other halogenated compounds analyzed. Therefore, the only halogens analyzed and reported in this study are Freon 11 and 12.

Table D-1. Contamination Study of Zero Air Stored in Tedlar Bags

Condition	Concentration				
	Cylinder Analysis	Q.C. 1	Q.C. 2	Q.C. 3	Q.C. 1*
Date Filled	5-13-76	5-13-76	6-7-76	5-20-76	5-13-76
Date Analyzed	5-13-76	5-13-76	6-11-76	6-14-76	6-17-76
Elapsed Time (days)	0	0	4	25	37
Ethane/ethylene[1/]	0.5	0.6	2.2	7.8	7.0
Propane	N.D.	0.1	0.5	1.8	0.2
Propylene	0.6	0.3	0.7	0.7	N.D.
Acetylene	N.D.	N.D.	N.D.	1.2	0.9
Butane	N.D.	0.2	1.5	0.4	0.4
1-Butene	N.D.	N.D.	0.6	N.D.	N.D.
Trans-2-Butene	N.D.	N.D.	N.D.	N.D.	N.D.
Isopentane	N.D.	N.D.	N.D.	0.2	N.D.
Freon 11[2/]	N.D.	N.D.	9.9	9.5	15.0
Freon 12	N.D.	N.D.	N.D.	N.D.	N.D.
Tricholoroethane	42.8	41.3	43.4	35.7	29.8
Carbon Tetrachloride	N.D.	N.D.	5.0	6.3	5.3
Tetrachloroethylene	N.D.	N.D.	417.0	44.3	205.0

*Q.C.1 was reanalyzed 37 days after filling.

[1/] Concentration = ppbV

[2/] Concentration = pptV

N.D. = non-detectable, < 0.1 ppbV

To examine the storage capability of the Tedlar bags, a blend of three hydrocarbon mixtures (acetylene, 1-butene, and trans-2-butene) was used to fill Q.C. bags in the field. The concentration for each hydrocarbon blended into the bag by dilution of a standard cylinder containing these hydrocarbons was approximately 71 ppbV. Q.C. 4 was blended at RTI, analyzed and transported to the field. Six additional Q.C. bags were blended using the same gases and procedure at the St. Louis field site immediately prior to the launch of DaVinci II. It is estimated that the blending accuracy for these bags under field conditions was ± 10 percent. These bags were then returned to RTI for analysis with elapsed times of 10 to 36 days between filling and analysis. Results of this study are presented in Table D-2.

Table D-2. Stability of Acetylene, 1-Butene, and Trans-2-Butene in Tedlar Quality Control Bags

Condition/ Constituent	Concentration*						
	QC-4	QC-5	QC-6	QC-7	QC-8	QC-9	QC-4**
Date Blended	5-13-76	6-07-76	6-07-76	6-07-76	6-07-76	6-07-76	5-13-76
Date Analyzed	5-13-76	6-17-76	6-17-76	6-18-76	6-30-76	6-30-76	6-18-76
Elapse time in days	0	10	10	11	23	23	36
Ethane/ethylene	1.7	2.9	2.2	9.6	6.8	1.9	116.6
Propane	N.D.	0.8	0.2	0.4	0.4	0.4	8.5
Propylene	0.5	0.5	N.D.	0.6	0.8	0.3	2.4
Acetylene	55.3	65.3	65.8	66.8	58.3	55.2	61.4
Butane	0.3	0.5	0.7	1.6	0.9	0.4	10.5
1-Butene	74.5	76.4	72.3	74.1	67.2	66.9	69.9
Trans-2-Butene	68.6	72.5	69.8	70.3	64.0	61.7	63.9
Isopentane	N.D.	N.D.	N.D.	N.D.	1.0	0.4	6.9

* Concentration = ppbV

** Sampling bag leaked.

The data in Table D-2 show that the stability of acetylene, 1-butene, and trans-2-butene was quite good in Tedlar bags for up to 23 days. The deviation of the analysis results is within the estimated accuracy for blending of the mixtures in most cases. It should be noted that the matrix in which these compounds were blended was zero air that was free of hydrocarbons and other reactive pollutants. Changes in the matrix, i.e., ambient air for field samples may have some effect on stability of collected field samples.

The data obtained in this study substantiate previously reported work regarding sampling of hydrocarbons using Tedlar bags in the C_2-C_5 range (Ref. D-1). In summation, results of the quality control program indicate that Tedlar bags were satisfactory for collection of hydrocarbons in the C_2-C_5 range and Freon 11 and 12, when samples were protected from the sunlight and analyzed within two weeks. Sampling bags fabricated from Tedlar were not satisfactory for the collection of other halogenated compounds.

D-1. Denyszyn, R. B., L. T. Hackworth, P. M. Grohse, and D. E. Wagoner, "Hydrocarbon and Halocarbon Measurements: Sampling and Analysis Procedure." Presented at the International Conference on Photochemical Oxidant Pollution and Its Control, Raleigh, North Carolina, September 12-17, 1976.